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ABSTRACT

This booklet, one of a series of 17 developed at Prince George's Community College, Largo, Maryland, provides an individualized, self-paced undergraduate organic chemistry instruction module designed to augment any course in organic chemistry but particularly those taught using the text "Organic Chemistry" by Morrison and Boyd. The entire series of modules covers the first 13 chapters of the Morrison-Boyd text in great detail. Each module has been provided with from one to three audiotapes, available from Prince George's Community College, to provide students additional explanations of particular concepts. Each module includes a self-evaluation exercise, a reference guide, worksheets to be completed with the audiotapes, answer sheets for the worksheets, a progress evaluation, an answer sheet for the self-evaluation exercise, an introduction to the topic covered by the module, and student performance objectives for the module. The topic of this module is alkenes-reactions 2: free radical additions and substitutions, hydrogenation, polymerization and oxidation. (SL)

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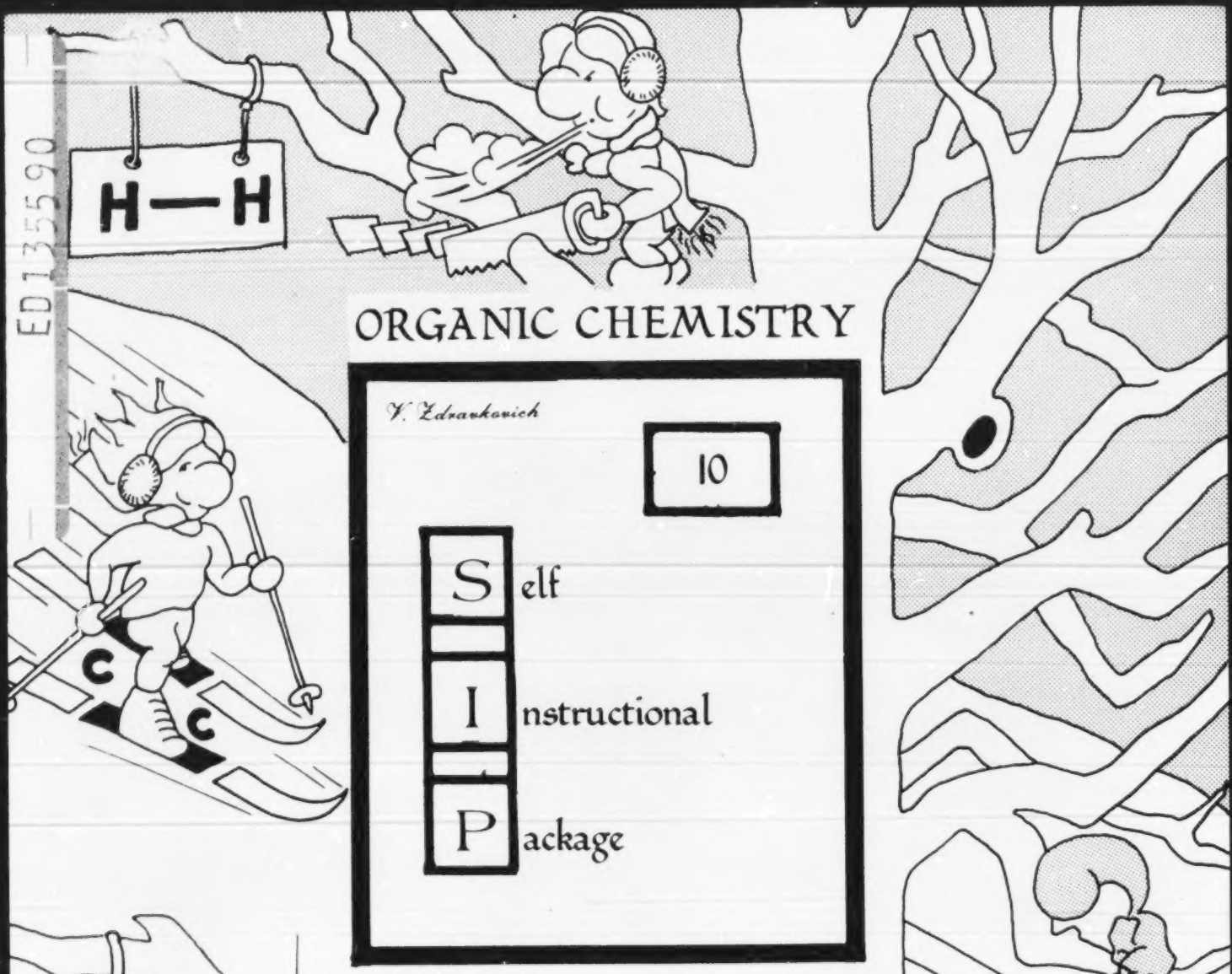


ORGANIC CHEMISTRY

V. Zdravkovich

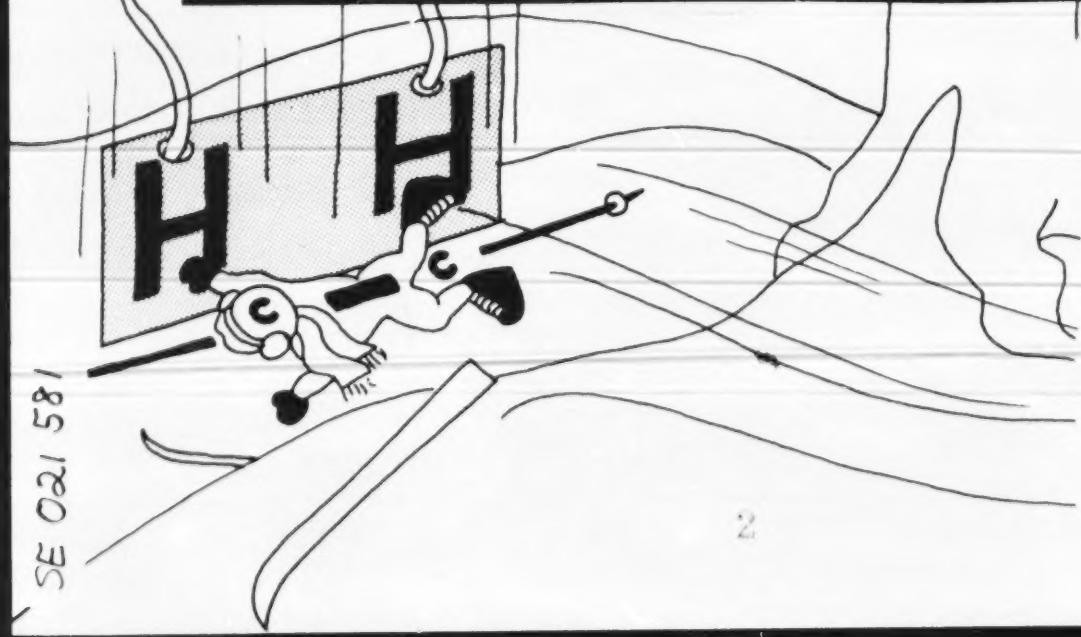
10

S elf

I nstructional

P ackage

ALKENES-REACTIONS 2



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SE 021 581

Self Instructional Sequence in

ORGANIC CHEMISTRY

"Copr.," V. Zdravkovich 1976

Self Instructional Package No. 10
Form A - List of Objectives

ALKENES - REACTIONS II

FREE RADICAL ADDITIONS AND SUBSTITUTION, HYDROGENATION, POLYMERIZATION AND OXYDATION

DEFINITIONS -

The student will be able to define, explain and illustrate with appropriate examples the following terms: RESONANCE, HYPERCONJUGATION, DELOCALIZATION OF ELECTRONS, ANTI MARKOVNIKOV'S RULE, PEROXIDE EFFECT, POLYMER, POLYMERIZATION, HETEROGENEOUS CATALYSIS, HOMOGENEOUS CATALYSIS, CHEMISORPTION, HEAT OF HYDROXYLATION, DIOL, GLYCOL.

REACTION MECHANISMS -

The student will be able to write the step by step mechanism and explain different aspects of: free radical addition reactions, free radical substitution reaction, free radical polymerization reactions, carbonium ion or cation polymerization.

REACTIONS -

The student will be able to write the balanced reactions for hydrogenation, ozonolysis, hydroxylation and halogen substitution in alkenes.

The student will be able to predict the major products in the peroxide catalyzed reaction of an alkene with carbon tetrahalide, haloform or other halo derivatives of methane. Given the reactants and the products, the student will be able to identify the necessary reagents.

The student will be able to write the reactions for the mild and vigorous oxidation reactions of alkenes with various reagents.

The student will be able to predict the products in different polymerization reactions.

The student will be able to identify the original akene from the given products of a vigorous oxidation.

REACTION SYNTHESIS -

The student will be able to write all the steps in a laboratory synthesis of a diol or different halo derivatives starting with methane. (This requires utilization of the knowledge acquired in the previous units)

The student will be able to identify all the compounds in a given multi-step synthetic scheme. (This also requires utilization of the knowledge acquired in the previous units)

Self Instructional Package No. 10
Form B - Self Evaluation Exercise

ALKENES - REACTIONS II

Identify the statements below as true or false by placing a capital T or F in the space provided.

1. _____ The function of the catalyst in the hydrogenation reaction is to lower the energy of the activation.

2. _____ Heat of hydrogenation is the heat used when one mole of an alkene is hydrogenated.

3. _____ Chemsorption is adsorption that involves chemical bonding.

4. _____ Catalysts used in the hydrogenation reaction interact with hydrogen and consequently hydrogen is activated.

5. _____ In the anti Markovnikov addition hydrogen adds to the doubly bonded carbon with less hydrogens.

6. _____ Branching at the double bond decreases the stability of alkenes.

7. _____ The most reactive hydrogen in an alkene is the vinylic hydrogen.

8. _____ Free radical addition of HBr complies with the Markovnikov's rule.

9. _____ High heat of hydrogenation indicates low stability of an alkene.

10. _____ Hyperconjugation is the delocalization of electrons involving σ bond orbitals.

Blacken out the correct answer or answers in each question:

11. From the given heats of hydrogenation for alkene A and B select the correct statements below:

    Alkene A: Heat of hydrogenation is 36 kcal/mole

    Alkene B: Heat of hydrogenation is 38 kcal/mole

    a) Alkene A is more stable than Alkene B
    b) Alkene B is more stable than Alkene A
    c) Alkene A possesses more energy than Alkene B
    d) Alkene B possesses more energy than Alkene A

12. In the free radical polymerization of propylene the first attacking alkyl species is:

a) $R-CH_2-CH_2-CH_2^{\bullet}$

b) $R-CH_2-CH_2-CH_2^{+}$

c) $R-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2^{\bullet}$

d) $R-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}^{\bullet}$

13. The great stability of the alkyl free radical is due to:

a) the delocalization of the electrons over three π orbitals.

b) the resonance stabilization energy.

c) overlap of the π orbitals of the double bond with the π orbital having the unpaired electron.

d) the hyperconjugation.

14. The major product in the reaction of 2-butene with $CBrCl_3$ in presence of peroxide is:

a) 1,1,3-tricholoro-1-bromo-2-methyl butane

b) 1,1,1-tricholoro-3-bromo-2-methyl butane

c) 1,1,1-tricholro-3-bromo pentane

d) 1,1,3-tricholoro-3-bromo pentane

15. The major compound produced in a reaction of 2-methyl-2-butene with bromoform in presence of peroxide is:

a) 1,1,1-tribromo-2,3-dimethyl butane

b) 1,1,1-tribromo-3-methyl pentane

c) 1,1,1-tribromo-2,2-dimethyl butane

d) 1,1,1-tribromo-4-methyl pentane

16. When 5-methyl-2-hexene is allowed to react with bromine in limited amount and at high temperature the major production is:

a) 2,3-dibromo-5-methyl hexane

b) 1-bromo-5-methyl-2-hexene

c) 3-bromo-5-methyl-2-hexene

d) 5-bromo-5-methyl-2-hexene

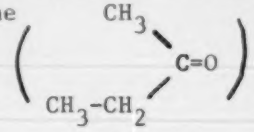
17. The function of NBS in the free radical bromination of alkene is:

    a) to catalyze the reaction.

    b) to provide a constant and low concentration of bromine during the reaction.

    c) to initiate the reaction.

    d) to provide high concentration of bromine in the reaction.

18. The reagent required to convert 2-methyl-1-butene into carbon dioxide and methyl ethyl ketone  is:

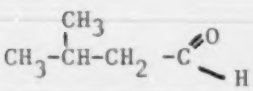
    a) O_3 ; H_2O, Zn

    b) $KMnO_4$, ao

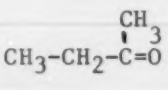
    c) peroxyformic acid

    d) hot $KMnO_4$

19. Alkene that yields compounds I and II, ozonolysis is:



I



II

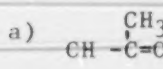
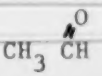
    a) 2,7-dimethyl-4-heptene

    b) 3,6-dimethyl-3-heptene

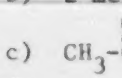
    c) 3,5-dimethyl-3-heptene

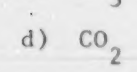
    d) 2,7-dimethyl-3-heptene

20. The reaction of 2-methyl-2-butene with peroxyformic acid followed by hydrolysis results in the formation of:

    a)  and 

    b) 2-methyl-2,3-butane diol

    c)  and CH_2COOH

    d) CO_2 and 

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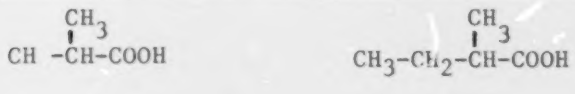
21. Alkene thatyields compounds I and II upon vigorous oxidation with $KMnO_4$ is:



I II

a) 2-methyl-2-hexene

b) 2,5-dimethyl-3-heptene

c) 2,6-dimethyl-3-heptene

d) 2,5-dimethyl-3-heptene

22. The reagents that can be used to convert butane into 3,4-dimethyl-3,4-hexane diol are:

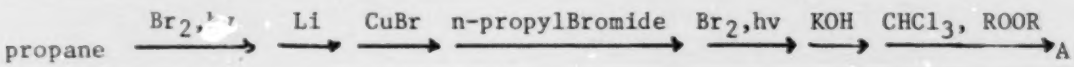
a) Na, KOH, $KMnO_4$, H_2O

b) Br_2,hv; Na; Br_2,hv; KOH; $KMnO_4$; aq

c) Br_2,hv ; Li ; CuBr; 2-bromobutane; Br_2,hv; KOH; peroxyformic acid, H_2O

d) Br_2,hv ; Na ; KOH ; peroxyformic acid, water

23. Identify the compound A in the multi-step synthesis scheme below



a) 1,1,1-tricholoro-2,2-dimethyl pentane

b) 1,1,1-tricholo-2-ethyl-pentane

c) 1,1,1-trichloro-3-methyl-2-ethyl-butane

d) 1,1,1-tricholoro-2,2,3-trimethyl-butane

Self Instructional Package No. 10
Form C - Reference Guide

ALKENES - REACTIONS II

The Reference Guide should be used in conjunction with Form B or the Self Evaluation Exercise. The references give the Correlation between the questions in Form B and the available material in the textbook and in the form of tapes.

Questions 1, 2, 6, 9, 11	Chapter 6, Sections 3, 4
Questions 5, 8	Chapter 6, Sections 7, 17
Question 7	Chapter 6, Section 22
Question 10	Chapter 6, Section 28
Question 12	Chapter 6, Section 19
Question 13	Chapter 6, Sections 23, 24, 25, 26, 27
Questions 14, 15, 23	Chapter 6, Section 18
Questions 16, 17	Chapter 6, Section 21,22
Questions 18,19,20,21,22	Chapter, 6, Sections 20, 29

For Questions: 5,7,8,10,13,14,15,16,17,23, additional explanations, examples and study questions can be found in Tape 1 - with the accompanying worksheet and answer sheet.

For Questions: 1,2,3,4,6,9,11,12,18,19,20,21,22 additional explanations, examples and study questions can be found in Tape 2 - with the accompanying worksheet and answer sheet.

What harm in getting knowledge even from a sot, a pot, a fool, a mitten or an old slipper?
Rabelais (1532)

Self Instructional Package No. 10
Tape I - Work Sheet

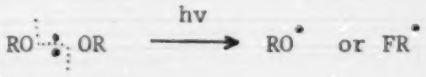
ALKENES - REACTIONS

Free Radical Addition and Substitution; Resonance; Hyperconjugation

Chain Initiating Steps

Example No. 1 - Free Radical Mechanism for the Anti-Markovnikov Addition of HBr to Alkene

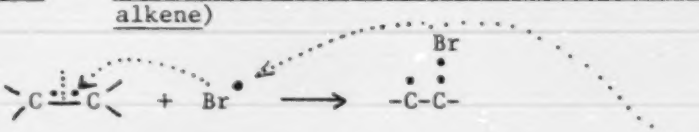
Step 1 - Formation of the initial free radical (homolytic cleavage of the O-O bond in peroxides)



Step 2 - Formation of the bromine atom or bromine radical

Chain Propagating Steps

Step 3 - Formation of the alkyl free radical (addition of Br• to the alkene)



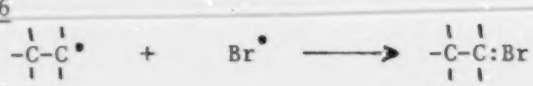
Step 4 - Reaction of the alkyl F.R. with HBr (abstration of H atom from HBr)

Steps 3, 4, 3, 4, 3, 4 .....

Chain Terminating Steps

Step 5

Step 6



SIP No. 10
Tape I - Work Sheet

Example No. 2 - Free Radical Mechanism for the Addition of HBr to Propene and Isobutene

Propene Isobutene

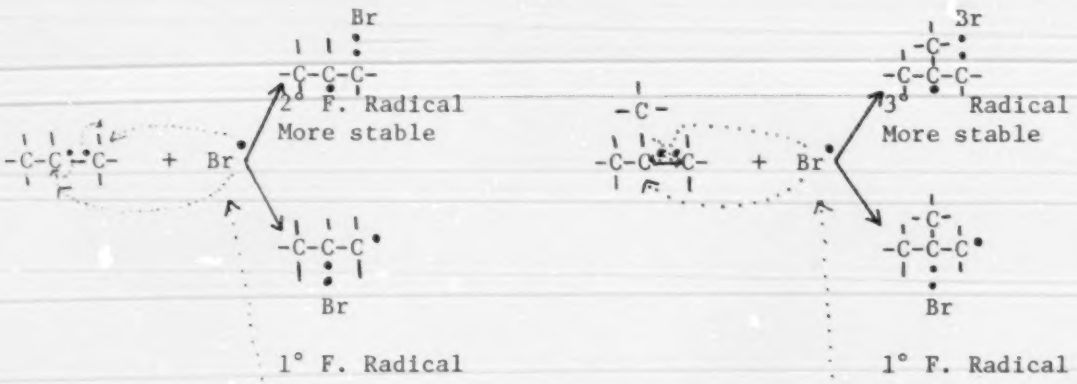
Step 1 - Dissociation of the Peroxide

RO : OR ⟶ RO• or FR•

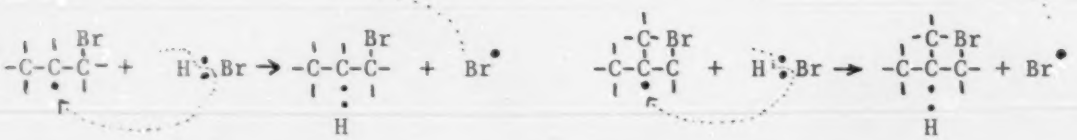
Step 2 - Formation of the Bromine Radical

Fr• + H : Br ⟶ FRH + Br•

Step 3 - Addition of Br• to the Alkene and the Formation of Alkyl Free Radical



Step 4 - Reaction of the Alkyl Free Radical with HBr



Overall Reactions:

C=C-C + HBr —Peroxide, hv⟶ C-C-C (Br) 1-bromo propane

C (C=C-C) —Peroxide, hv⟶ C (C-C-C-Br) 1-bromo-2-methyl propane

Anti-Markovnikov Addition: H from HBr adds to the C of the double bond that has LESS hydrogens.

11

SIP No. 10
Tape I - Work Sheet

Assignment No. 1

Write the step by step mechanism for the peroxide catalyzed addition of HBr to 3,3-Dimethyl-1-Butene.

Assignment No. 2

Draw the structures and name the products in the following reactions:

3,3-Dimethyl-1-butene $\xrightarrow{HBr}$

2-methyl-2-butene $\xrightarrow{HBr}$

2-methyl-2-butene $\xrightarrow{HBr,\ Peroxide}$

3-methyl-1-pentene + HBr $\xrightarrow{Peroxide}$

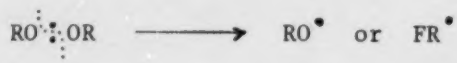
3-methyl-1-pentene + HBr $\longrightarrow$

SIP No. 10
Tape I - Work Sheet

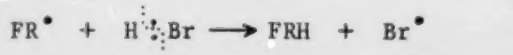
Assignment No. 3

Confused Clyde was asked to write the step by step mechanism for the addition of HBr to 3-methyl-1-pentene in presence of peroxide. His answer is given below. Examine his answer and rectify his state of confusion.

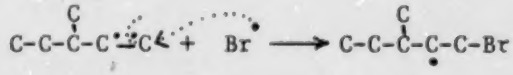
Step 1



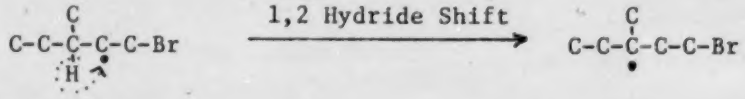
Step 2



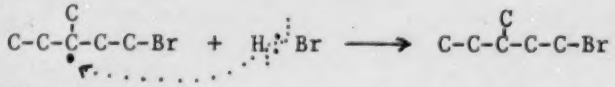
Step 3



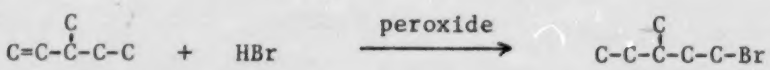
Step 3a



Step 4



Overall Reaction:



SIP No. 10
Tape I - Work Sheet

Assignment No. 4

Saturated Sam was asked to write the step by step mechanism for the peroxide catalyzed addition of HBr to 3-methyl-2-pentene. Examine his answer and make any necessary corrections.

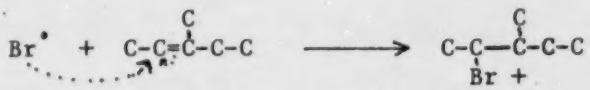
Step 1

$$ROOR \xrightarrow{h\nu} RO^{\bullet} \text{ or } Fr^{\bullet}$$

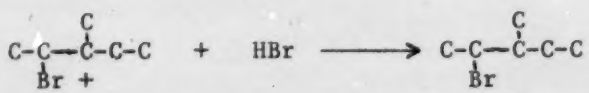
Step 2

$$Fr^{\bullet} + H{:}Br \longrightarrow FRH + Br^{\bullet}$$

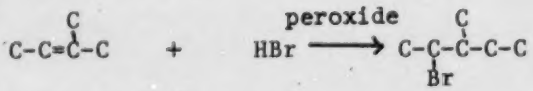
Step 3



Step 4



Overall Reaction:



Assignment No. 5

Forgetful Frieda was given the same question as that asked of Saturated Sam. Her answer is given below. Are there any corrections necessary? If so, write them below.

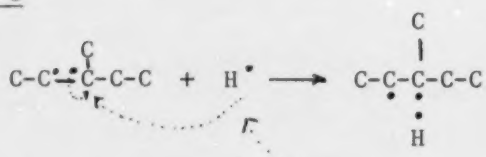
Step 1

$$ROOR \xrightarrow{h\nu} RO^{\bullet} \text{ or } FR^{\bullet}$$

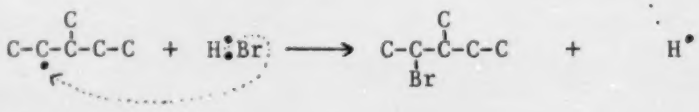
Assignment No. 5 (continued)

Step 2

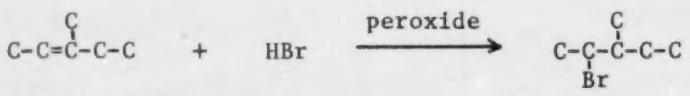
Step 3



Step 4



Overall Reaction:



Assignment No. 6

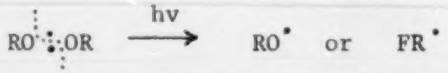
a) Calculate the ΔH values for the two chain propagation steps of the free radical addition of hydrogen fluoride, hydrogen chloride, hydrogen bromide and hydrogen iodide to propene.

b) Suggest a possible reason why the peroxide effect is observed for HBr but not for the other hydrogen halide.

SIP No. 10
Tape I - Work Sheet

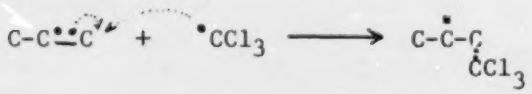
Example No. 3 - Free Radical Addition of CCL_4 to Propene

Step 1 - Homolytic Cleavage of the O-O Bond in Peroxides



Step 2

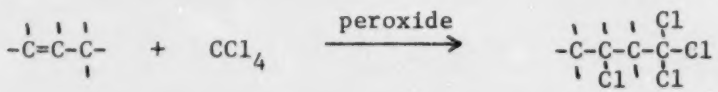
Step 3 - Formation of the Alkyl F.R. - Addition of the Trichloro Radical From Step 2 to the Alkene



Step 4 - Reaction of the Alkyl Free Radical with CCl_4

Steps 3, 4, 3, 4, 3, 4, ...

Overall Reaction:



1,1,1,3-trichlorobutane

SIP No. 10
Tape I - Work Sheet

Assignment No. 7

When $CBrCl_3$ is added to isobutene in presence of peroxide, 1,1,1-trichloro-3-bromo-3-methyl butane is formed as the major product. Propose a mechanism for the reaction.

Assignment No. 8

Propose a mechanism for the peroxide catalyzed reaction of 2-methyl-1-butene with tribromo methane in which 1,1,1-tribromo-3-methyl pentane is formed.

SIP No. 10
Tape I - Work Sheet

Assignment No. 9

Draw the structure and name the products in the following reactions:

3-methyl-2-pentene + $CHCl_3$ $\xrightarrow{\text{peroxide}}$

2,3,5-trimethyl-3-hexene + CBr_4 $\xrightarrow{\text{peroxide}}$

2,5-dimethyl-3-hexene + $CHBr_3$ $\xrightarrow{\text{peroxide}}$

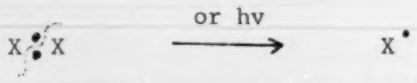
Assignment No. 10

Propose a mechanism for the peroxide catalyzed reaction of 1-butene with carbontetrachloride that will account for the formation of both the major product or 1,1,1,3-tetrachloropentane and 1,1,1,5-tetrachloro-3-ethyl-heptane.

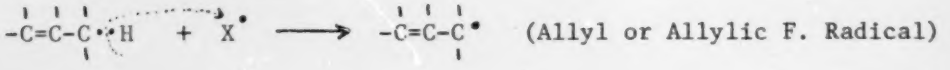
SIP No. 10
Tape I - Work Sheet

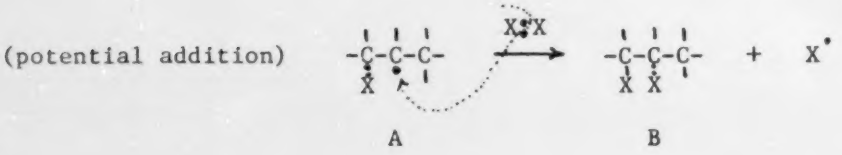
Example No. 4 - Free Radical Mechanism for the Halogen Substitution in Alkenes

Step 1 - Homolytic Cleavage of the Halogen Molecule



Step 2 - Abstraction of the H• by X• and the Formation of the Alkyl Free Radical





Step 3

Steps 2, 3, 2, 3, 2, 3,....

Addition of X_2 (Ionic) is favored by: low temperature, absence of light, high concentration of halogen, liquid phase

Substitution of X_2 - (Free Radical) is favored by: high temperature, presence of light, low concentration of halogen, gaseous phase.

Low concentration of bromine is often supplied by the NBS.

N-Bromosuccinimide (NBS)

Succinimide

SIP No. 10
Tape I - Work Sheet

Example No. 5

Bond Dissociation Energies $(A\text{-}B \longrightarrow A^{\bullet} + B^{\bullet})$

$H_2C = CH\text{-}H$	104 kcal/mole	$(CH_3)_3C\text{-}H$	91 kcal/mole
$H_3C\text{-}CH_2\text{-}H$	98 kcal/mole		
$H_2C = CH\text{-}CH_2\text{-}H$	88 kcal/mole		

Ease of abstraction of hydrogen atoms:

Allylic > 3° > 2° > 1° > Vinylic

Allylic Hydrogen Vinylic Hydrogen

Ease of formation of free radicals:

Allylic > 3° > 2° > 1° > Vinylic

Stability of free radicals:

Allylic > 3° > 2° > 1° > Vinylic

Assignment No. 11

Inert Irma was asked to draw the structure and name the major product in the reactions below. Examine her answer and make any necessary corrections.

5-methyl-2-hexene + Cl_2 $\xrightarrow{\text{heat}}$ 5-chloro-5-methyl - 2 - hexene

2-methyl-3-hexene + Br_2 $\xrightarrow{\text{NBS}}$ 3,4-dibromo-3-hexene

2-hexene $\xrightarrow{Br_2, CCl_4}$ 1,1,1-trichloro-3-bromo-2-methyl hexane

Assignment No. 11 (continued)

2-methyl propene $\xrightarrow{Br_2,\ hv}$ 1,2-dibromo-2-methyl propane

Example No. 6 - Resonance as applied to allyl radical

$CH_2{=}CH{-}\dot{C}H_2 \longleftrightarrow \dot{C}H_2{-}CH{=}CH_2$ Same structure, same arrangement of atoms in space, but different arrangement of electrons.

I II

Allyl free radical is the resonance hybrid of structures I and II

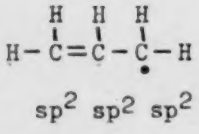
$CH_2{=}CH{-}\dot{C}H_2 \longleftrightarrow \dot{C}H_2{-}CH{=}CH_2 \longleftrightarrow CH_2\cdots CH\cdots CH_2$

Double Bond — Single Bond

Both bonds have identical length - hybrid bonds

C=C DOUBLE BOND < HYBRID BOND IN ALKYL RADICAL < C — C SINGLE BOND

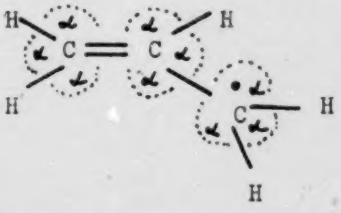
Example No. 7 - Orbital picture of the allyl radical



sp^2 sp^2 sp^2

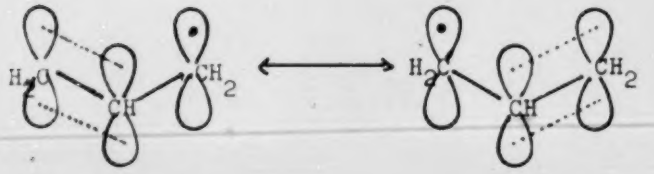
Hybridization

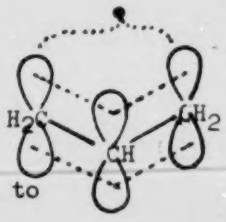
or



$\alpha = 120^\circ$

$CH_2{=}CH{-}\dot{C}H_2 \longleftrightarrow \dot{C}H_2{=}CH{-}CH_2$ equivalent to



equivalent to 

p Atomic Orbitals

SIP No. 10
Tape I - Work Sheet

Assignment No. 11 (continued)

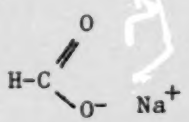
THE OVERLAP OF THREE P ORBITALS occupied by three electrons

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}H \xrightarrow{E = 98 \text{ kcal/mole}} CH_3\text{-}CH_2\text{-}CH_2^{\bullet} + H^{\bullet}$$

$$CH_2 = CH\text{-}CH_2\text{-}H \xrightarrow{E = 88 \text{ kcal/mole}} CH_2 = CH\text{-}CH_2^{\bullet} + H^{\bullet}$$

Assignment No. 12

Sodium Formate might be represented as:



Actual measurement shows that both carbon-oxygen bonds have equal length 1.27 A (carbon-oxygen single bond is 1.36 A; carbon-oxygen double bond is 1.23 A).

a) What is the better representation of the structure above?

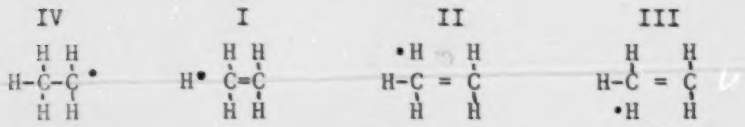
b) How can you explain the equal length of the two carbon-oxygen bonds?

c) Draw the orbital picture of the anion ($HCOO^-$) above.

SIP No. 10
Tape I - Work Sheet

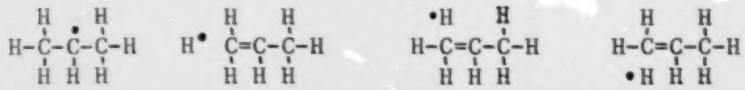
Example No. 8 - Hyperconjugation

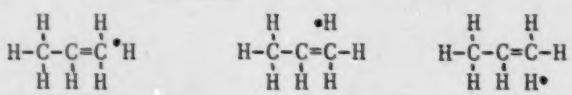
Resonance structures of ethyl free radical -



Hyperconjugation structures

Resonance structures of ispropyl free radical -





Hyperconjugation Structures

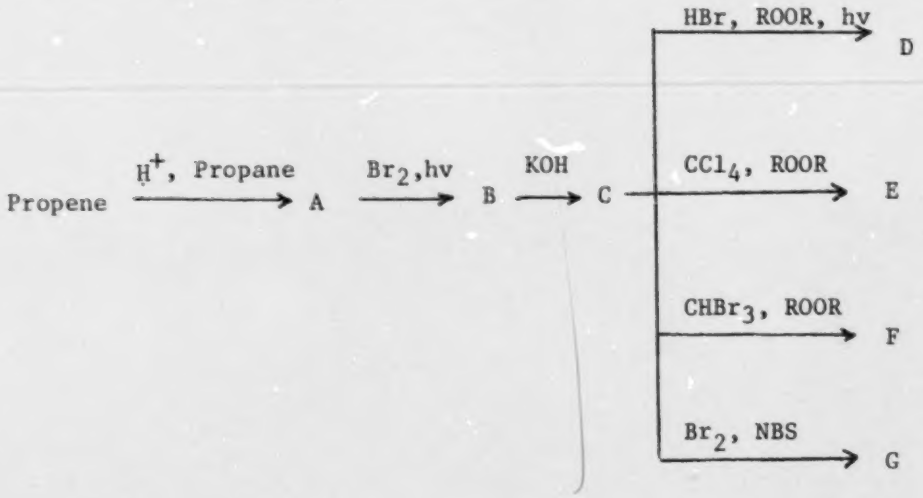
Assignment No. 13

Draw all the resonance structures for the tertiary butyl radical. Will it contain more or less Energy than the isopropyl free radical?

SIP No. 10
Tape I - Work Sheet

Assignment No. 14

Identify (draw structures and name) compounds A through G in the reaction sequence below.



Assignment No. 15

Identify all the steps in the laboratory synthesis of:

a) 4-bromo-2-methyl-2-pentene from 2-methyl pentane and

b) 1,1,1-trichloro-3-methyl butane from 2-methyl propane.

Self Instructional Package No. 10
Tape 1 - Answer Sheet

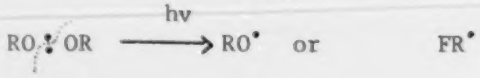
All is riddle, and the key to a riddle is another riddle. Emerson (1860)

ALKENES - REACTIONS

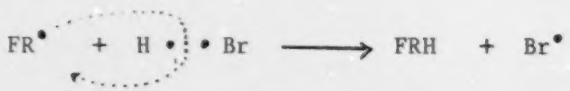
Free Radical Addition and Substitution; Resonance; Hyperconjugation

Assignment No. 1

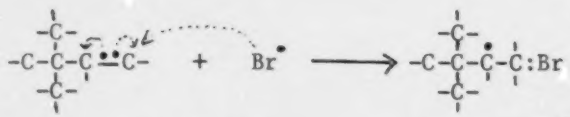
Step 1



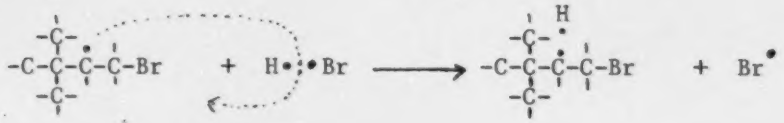
Step 2



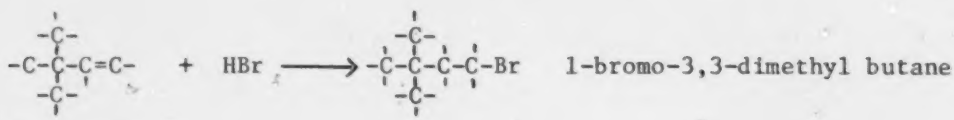
Step 3



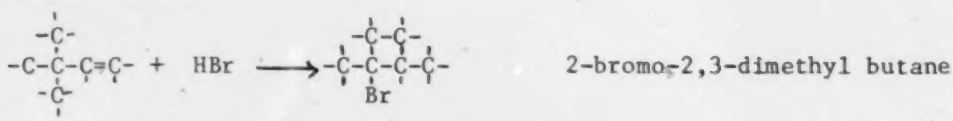
Step 4

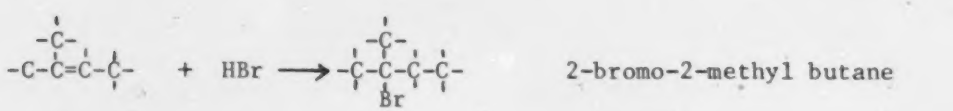


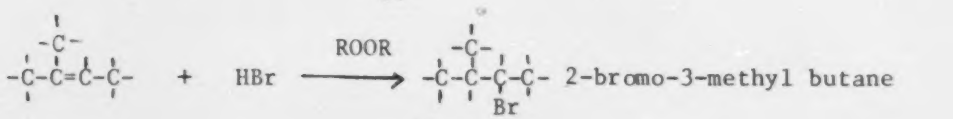
Overall Reaction:



Assignment No. 2

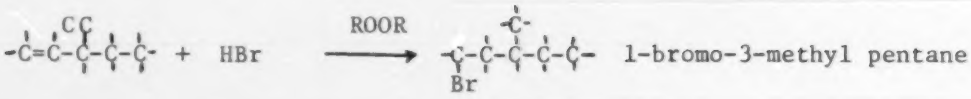


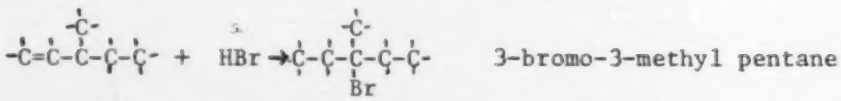




SIP No. 10
Tape I - Answer Sheet

Assignment No. 2 (continued)



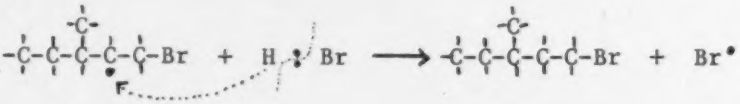


Assignment No. 3

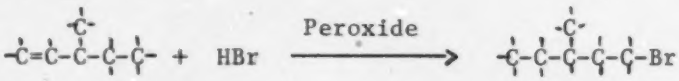
Steps 1, 2, and 3 are correct.

Step 3A does not exist, there is NO rearrangement in free radical reactions.

Step 4



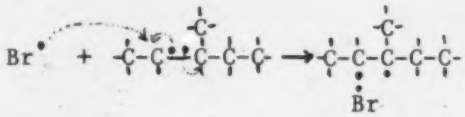
Overall Reaction:



Assignment No. 4

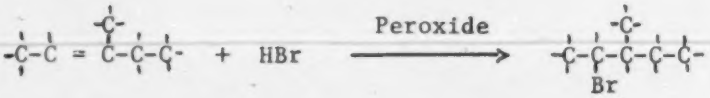
Steps 1, and 2 are correct.

Step 3



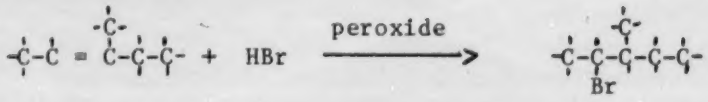
There are NO IONS in a free radical mechanism.

Step 4



SIP No. 10
Tape I - Answer Sheet

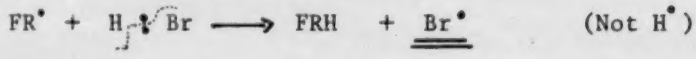
Overall Reaction:



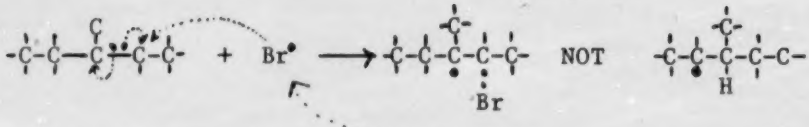
Assignment No. 5

Step 1 is correct.

Step 2

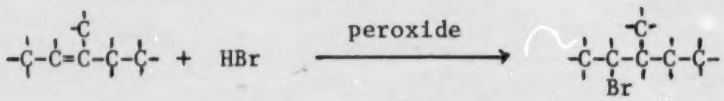


Step 3



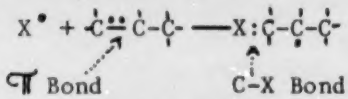
Step 4

Overall Reaction:



Assignment No. 6

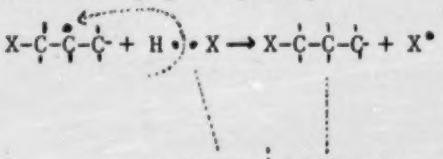
a)

	HX = HF	HX = HCl	HX = HBr	HX = HI
Chain Propagating Step I				
	ΔH=+68-105 ΔH=-37 kcal/mole (low E act)	ΔH=+68-82 ΔH=-14 kcal/mole (low E act)	ΔH=+68-69 ΔH=-1 kcal/mole (low E act)	ΔH=+68-55 ΔH=+13 kcal/mole (high E act)

SIP No. 10
Tape I - Answer Sheet

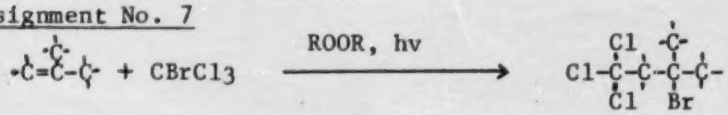
Assignment No. 6 (continued)

a) (continued)

	HX = HF	HX = HCl	HX = HBr	HX = HI
Chain Propagating Step II	ΔH=+136-95	ΔH=+103-95	ΔH=+88-95	ΔH=71-95
	ΔH=+41 kcal/mole	ΔH=8 kcal/mole	ΔH=-8 kcal/mole	ΔH=-24 kcal/mole
H-X Bond Cleaved / C-H Bond Formed	(high E act)	(high E act)	(low E act)	

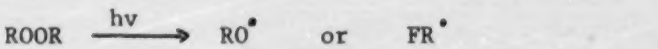
b) Only in the free radical addition of HBr to an alkene both steps have low activation energy and the reaction is energetically favored. HF, HCl, and HI will not add to an alkene via free radical mechanism.

Assignment No. 7



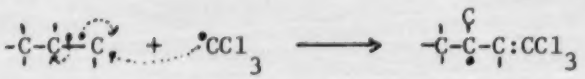
Mechanism:

Step 1

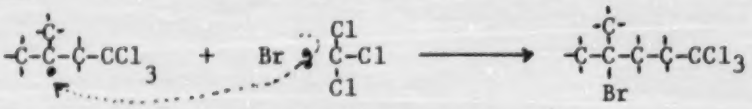


Step 2

Step 3 - Formation of the alkyl Free Radical (Addition of $^{\bullet}CCl_3$ to the alkene)



Step 4 - Reaction of the alkyl Free Radical with the reactant ($CBrCl_3$)

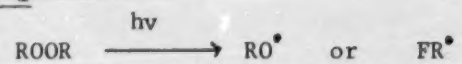


Then Steps 3, 4, 3, 4, 3, 4,....

SIP No. 10
Tape I - Answer Sheet

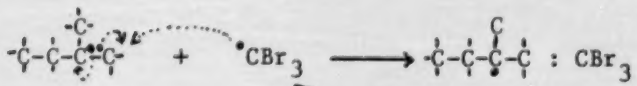
Assignment No. 8

Step 1

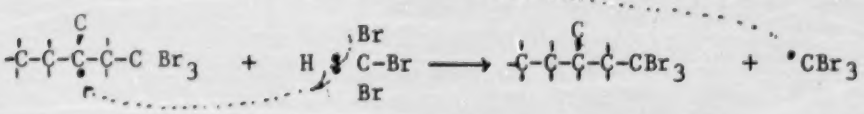


Step 2

Step 3 - Formation of the alkyl free radical (addition of the $^{\bullet}CB_3$ to the alkene)

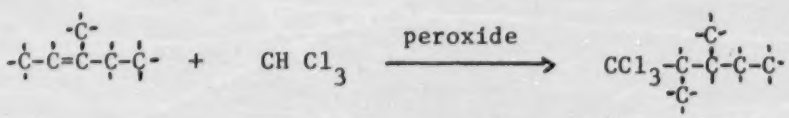


Step 4 - Reaction of the alkyl free radical with the reactant ($CHBr_3$)

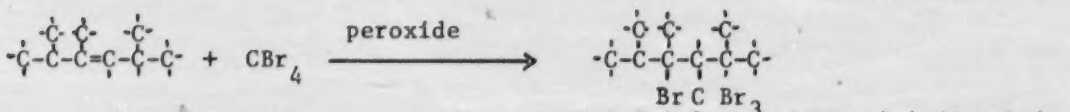


Then Step 3, 4, 3, 4, ...

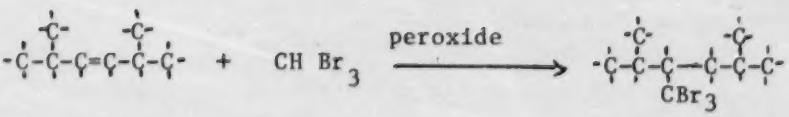
Assignment No. 9



1,1,1-trichloro-2,3-dimethyl pentane

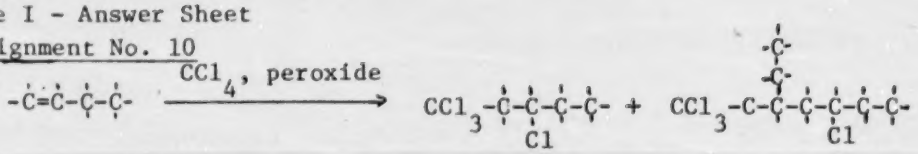


1,1,1,3-tetrabromo-3,4-dimethyl-2-isopropyl pentane



1,1,1-tribromo-4-methyl-2-isopropyl pentane

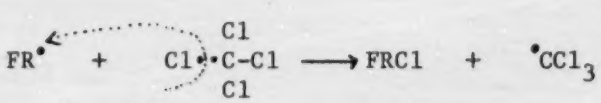
SIP No. 10
Tape I - Answer Sheet
Assignment No. 10



Mechanism: I (Major Product) II (By-product)

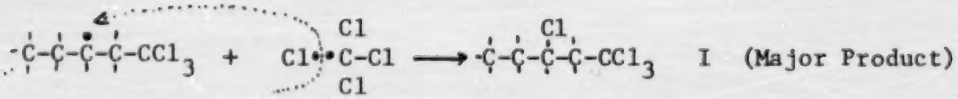
Step 1

Step 2

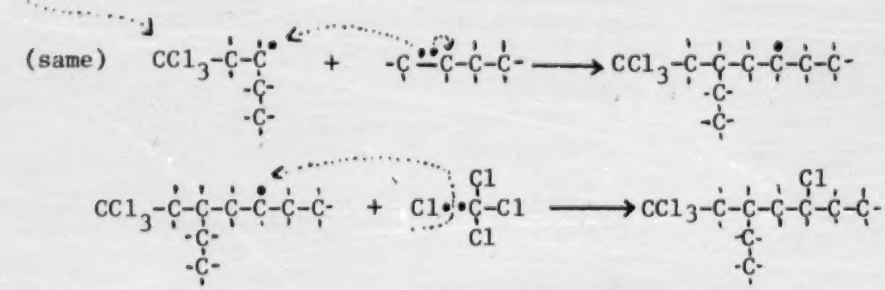


Step 3

Step 4

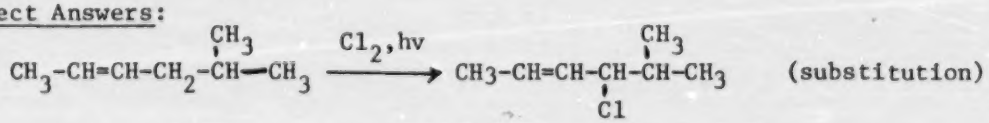


Other Possibility



Assignment No. 11

Correct Answers:

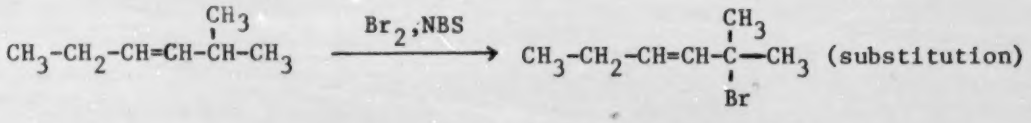


4-chloro-5-methyl-2-hexene

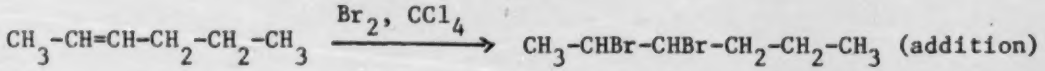
SIP No. 10
Tape I - Answer Sheet

Assignment No. 11 (continued)

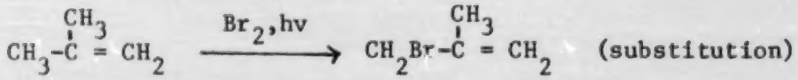
Correct Answers:



2-bromo-2-methyl-3-hexene



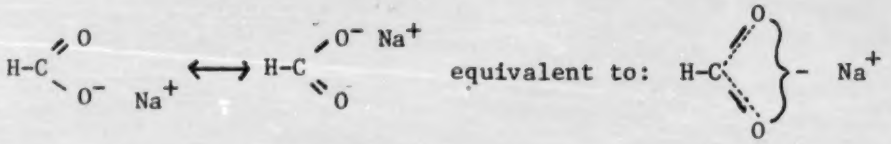
2,3-dibromo hexane



3-bromo-2-methyl propene

Assignment No. 12

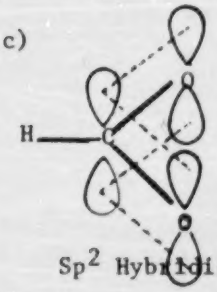
a)



I II III

b) Carbon-oxygen bond in III is a resonance hybrid of the carbon-oxygen single bond and the carbon-oxygen double bond.

c)

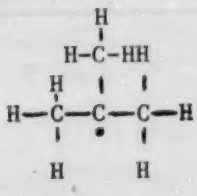


Sp^2 Hybridization on C - Flat Structure

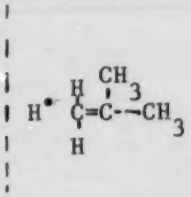
Sp^2 Hybridization

SIP No. 10
Tape I - Answer Sheet

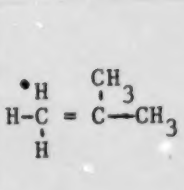
Assignment No. 13



X



I



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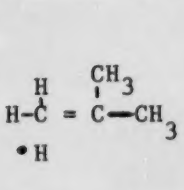
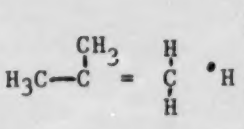


III



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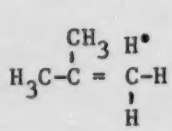
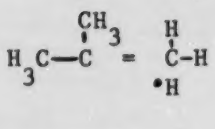


V



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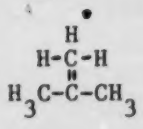
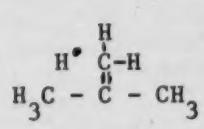
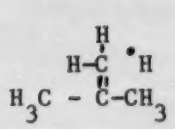


VII

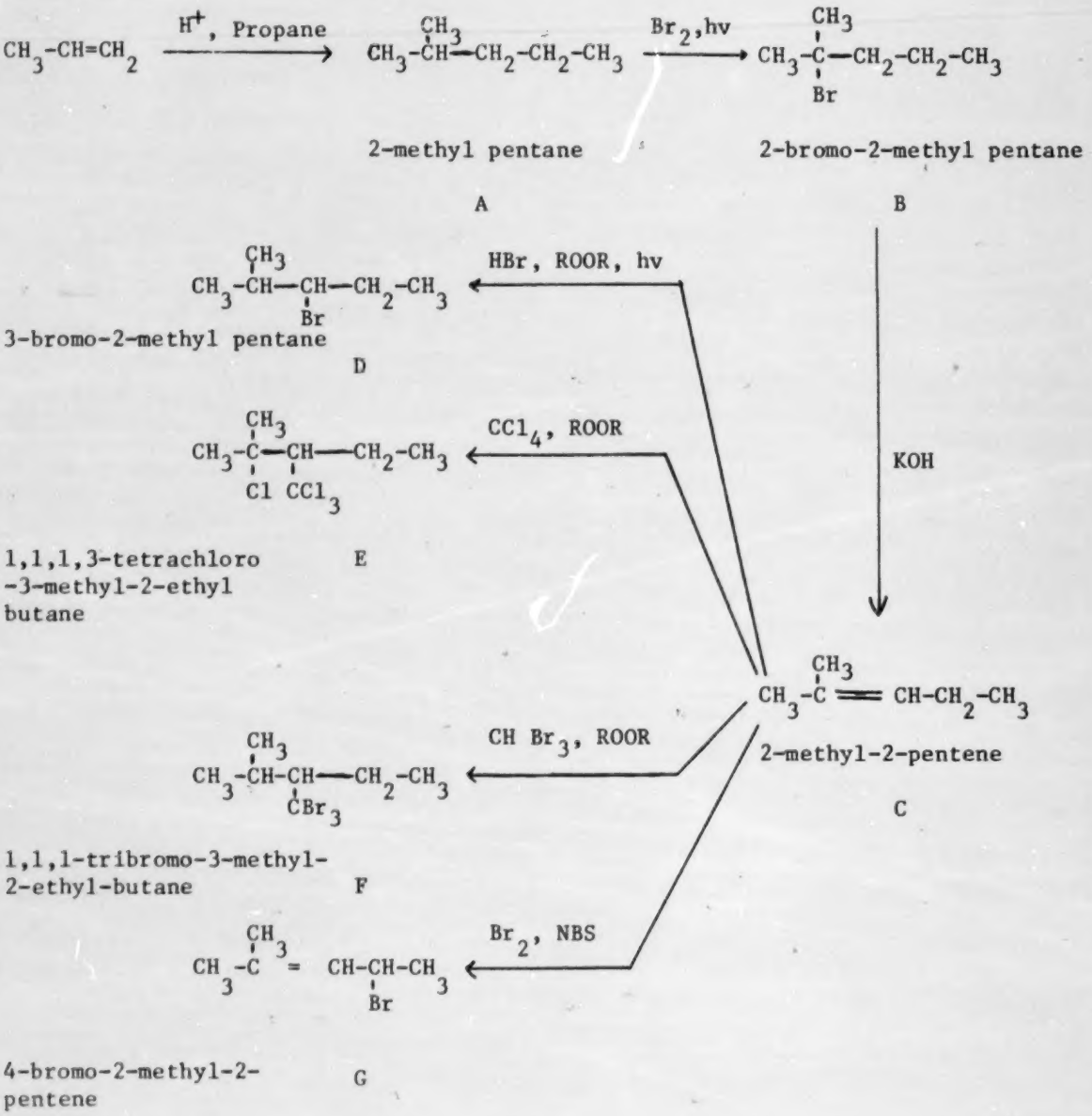


VIII



IX

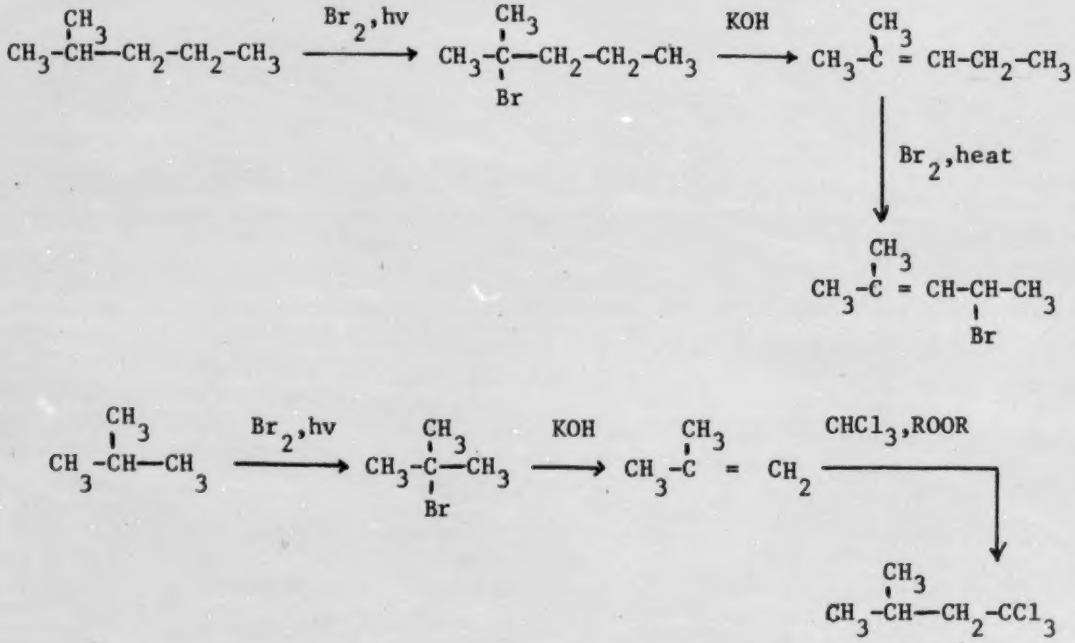
SIP No. 10
Tape I - Answer Sheet
Assignment No. 14



SIP No. 10
Tape I - Answer Sheet

Assignment No. 15

a)



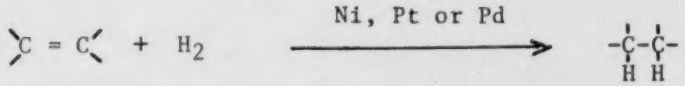
Self Instructional Package No. 10
Tape 2 - Worksheet

You have learnt something.
That always feels at first
as if you had lost something.
George Bernard Shaw (1905)

ALKENES - REACTIONS II

HYDROGENATION, POLYMERIZATION, OXIDATION

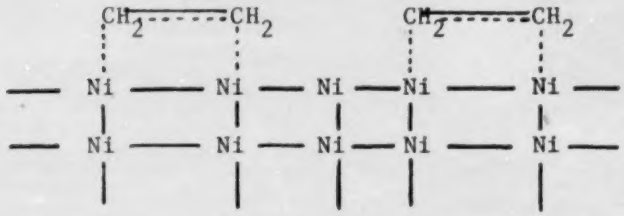
Example No. 1



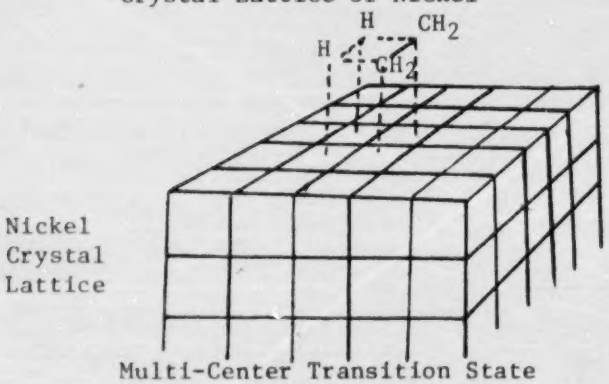
Alkene Alkane

Example No. 2 - Chemisorption

Chemisorption is adsorption that involves a formation of chemical bonds.

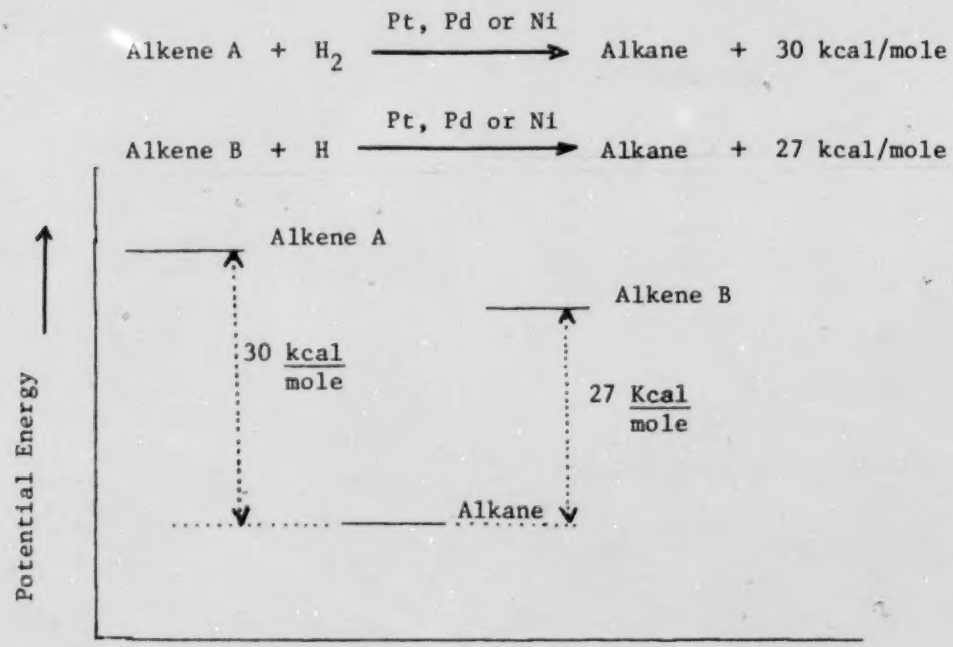


Crystal Lattice of Nickel

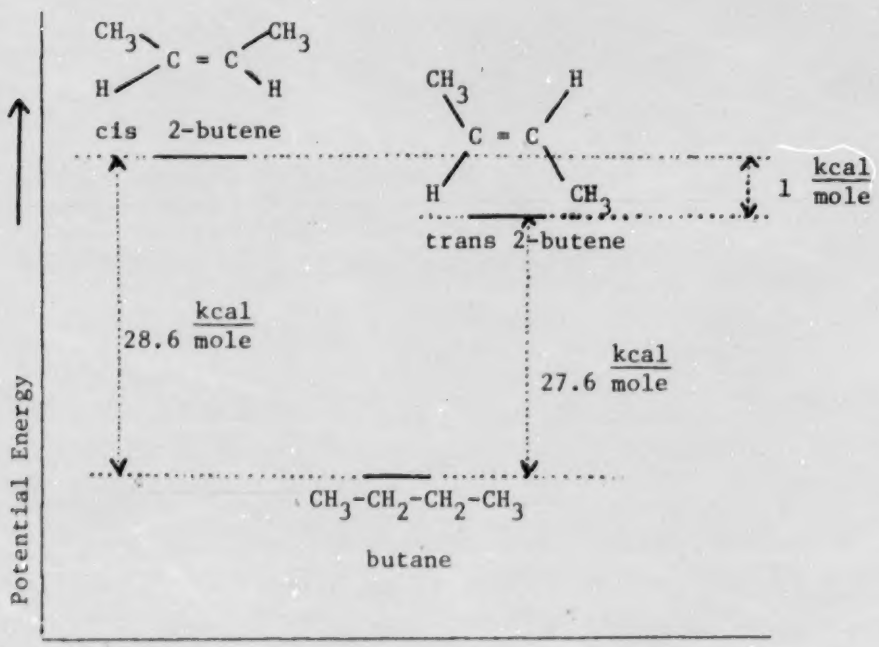


SIP #10
Tape 2 - Worksheet

Example No. 3 - Heats of hydrogenation and stability



Example No. 4 - Hydrogenation of cis and trans 2-butene



SIP #10
Tape 2 - Worksheet

Example No. 5 - Stability of alkenes based on the heats of hydrogenation values.

$R_2C{=}CR_2 > R_2C{=}CHR > R_2C{=}CH_2, RCH{=}CHR > RCH{=}CH_2 > CH_2{=}CH_2$

(Stability is inversely proportional to the heat of hydrogenation)

Assignment No. 1

The observed heat of hydrogenation of 2-methyl-1-butene is 28.5 kcal/mole and that of iron 2-pentene is 27.6 kcal/mole. Which of the two alkenes is more stable? _____

Assignment No. 2

Assign the following heats of hydrogenation to:

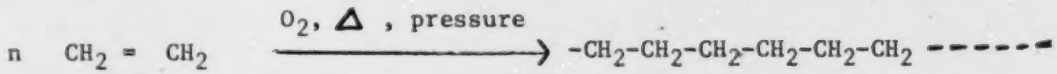
3,3-dimethyl-1-butene, 2,3-dimethyl-2-butene and 2,3-dimethyl-1-butene: 26.6, 30.3, 28 ical/mole. Identify the compound with maximum and minimum stability.

Assignment No. 3

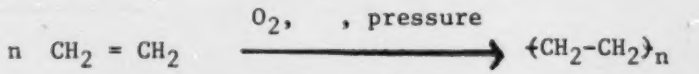
Assign the following heats of combustion to 1-pentene and cis and trans-2-pentene: 804,3, 806,9, 805,3 kcal/mole

SIP No. 10
Tape 2 - Work Sheet

Example No. 6



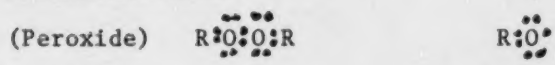
or in the abbreviated form

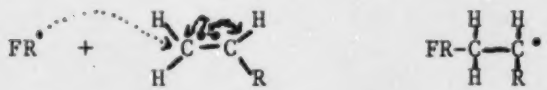


Ethylene — Polyethylene

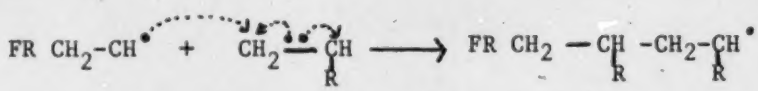
Example No. 7 - Free Radical Polymerization of Alkenes

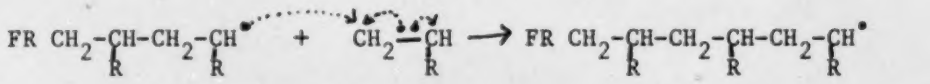
Chain initiation:





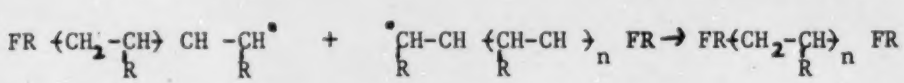
Chain Propagation:





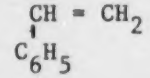
etc.

Chain Termination:



Assignment No. 4

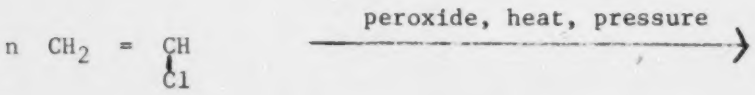
Write the step by step mechanism and the overall reaction for the polymerization of Styrene



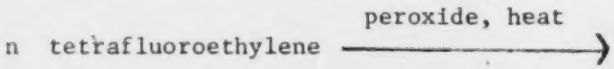
SIP No. 10
Tape 2 - Work Sheet

Assignment No. 5

Complete the reactions below, and supply the names of the polymer.

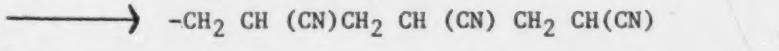


vinyl chloride

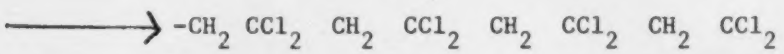


Assignment No. 6

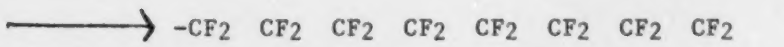
Identify the structure of the monomer from which each of the polymers below would most likely be made.



orlon (fibers, fabrics)



saran (packaging film, seat covers)



teflon (chemically resistant articles)

SIP NO. 10
Tape 2 - Worksheet

Assignment No. 7

Inert Irma was asked to write the chain initiating and the chain propagating steps for the free radical polymerization of propylene. Her answer is given below. Examine it carefully and identify her mistakes - if any.

Chain initiation:

$$ROOR \longrightarrow RO^{\bullet}$$

$$RO^{\bullet} + CH_3-CH=CH_2 \qquad RO-CH_2-CH-CH_2$$

Chain propagation:

$$RO-CH_2-CH-CH_2^{\bullet} + CH_2-CH=CH_2 \longrightarrow RO-CH_2-CH-CH_2-CH_2-CH-CH_2^{\bullet}$$

$$RO\ CH_2\ CH\ CH_2\ CH_2\ CH\ CH_2 + CH_2-CH=CH_2 \longrightarrow RO\ CH_2\ CH\ CH_2\ CH_2\ CH\ CH_2$$
$$\bullet CH_2\ CH\ CH_2 \quad \text{etc.}$$

Example No. 8 - Cationic Polymerization

Chain initiation:

$$CH_2=\underset{R}{CH} \xrightarrow{\text{Acid}} CH_3-\underset{R}{CH^+}$$

Acid (H_2SO_4 or HF or BF_3 or HCl etc)

Catalysts used: HF, H_2SO_4, BF_3, etc.

Chain propagation:

$$CH_3-\underset{R}{CH^+} + CH_2=\underset{R}{CH} \longrightarrow CH_3-\underset{R}{CH}-CH_2-\underset{R}{CH^+}$$

$$CH_3-\underset{R}{CH}-CH_2-\underset{R}{CH^+} + CH_2=\underset{R}{CH} \longrightarrow CH_3-\underset{R}{CH}-CH_2-\underset{R}{CH}-CH_2-\underset{R}{CH^+} \quad \text{etc.}$$

SIP No. 10
Tape 2 - Worksheet

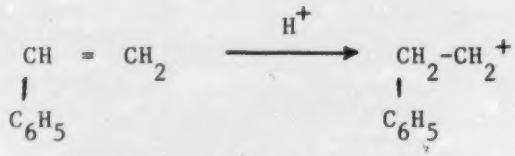
Example No. 8 (continued)

Chain termination:

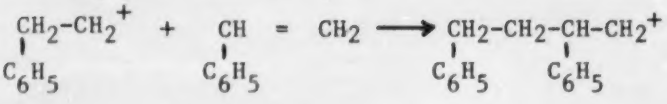
Assignment No. 8

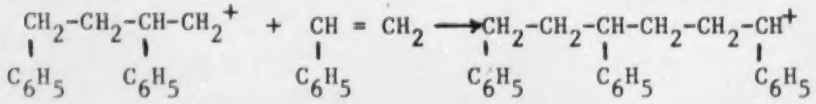
Confused Clyde was asked to write the chain initiating and the chain propagating steps for the cationic polymerization of styrene. His answer is given below. Rectify his state of confusion.

Chain initiation:



Chain propagation:





etc.

41

SIP No. 10
Tape 2 - Worksheet

Assignment No. 9

Can you suggest a reason why polymerization of propylene and other alkenes should take place in a way "head to tail" that yields a polymer with regularly alternating group?

Assignment No. 10

Curious Chloe tried to decide which of the two mechanisms presented below are correct. Can you help her? Explain your reasoning.

I. $H_2C = CHCl \xrightarrow{H^+} H_3C-\overset{+}{C}HCl$

$$H_3C-\underset{Cl}{\overset{+}{C}H} + H_2C = \underset{Cl}{CH} \longrightarrow H_3C-\underset{Cl}{CH}-CH_2-\underset{Cl}{\overset{+}{C}H}$$

$$H_3C-\underset{Cl}{CH}-CH_2-\underset{Cl}{\overset{+}{C}H} + H_2C=\underset{Cl}{CH} \longrightarrow H_3C-\underset{Cl}{CH}-CH_2-\underset{Cl}{CH}-CH_2-\underset{Cl}{CH} \quad \text{etc.}$$

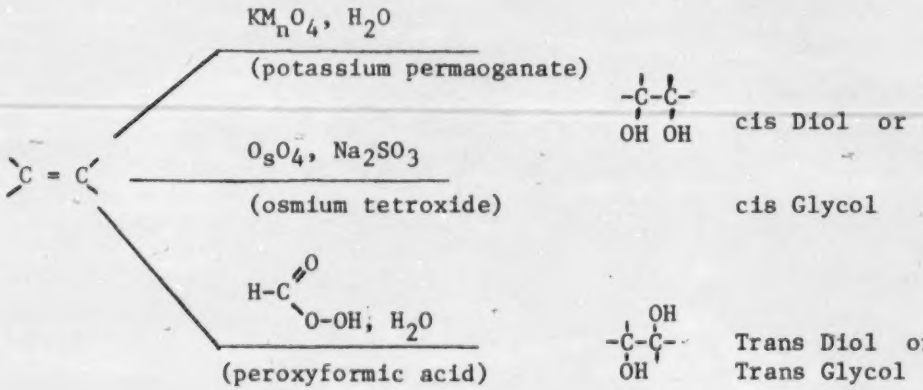
Assignment No. 10 (continued)

II. $H_2C{=}CH(Cl) + H^+ \longrightarrow CH_2{-}CH_2^+(Cl)$

$CH_2{-}CH_2^+(Cl) + HC{=}CH_2(Cl) \longrightarrow CH_2{-}CH_2{-}CH{-}CH_2^+(Cl,Cl)$

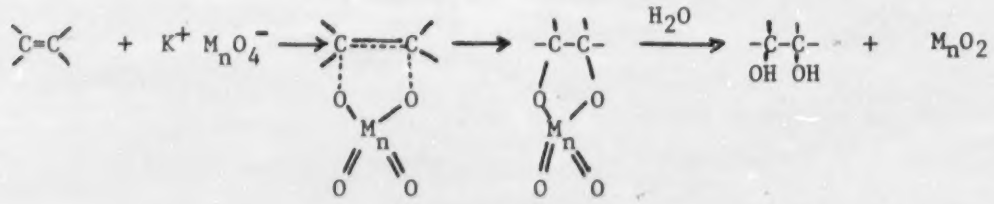
$CH_2{-}CH_2{-}CH{-}CH_2^+(Cl,Cl) + HC{=}CH_2(Cl) \longrightarrow CH_2{-}CH_2{-}CH{-}{-}CH_2{-}CH{-}CH_2^+(Cl,Cl,Cl)$ etc.

Example No. 9 - Mild oxidation



Example No. 10

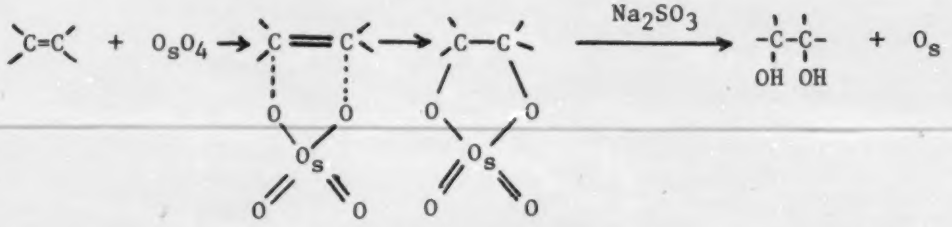
Hydroxylation with $KMnO_4$ (cis- cycloaddition Mechanism)



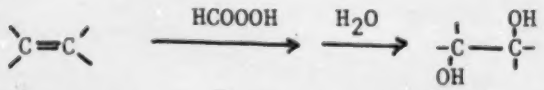
SIP No. 10
Tape 2 - Worksheet

Example No. 10 (continued)

Hydroxylation with O_sO_4 (cycloaddition Mechanism)



Hydroxylation with HCOOOH



trans diol

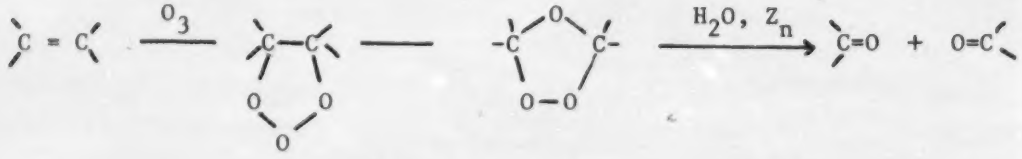
Example No. 11

$CH_2 = CH-CH_3 \xrightarrow{KM_nO_4,}$ $CH_2(OH)-CH(OH)-CH_3$ 1,2-propane diol (Propylene Glycol

$CH_3-CH= CH-CH_3 \xrightarrow{O_sO_4,\ Na_2SO_3}$ $CH_3-CH(OH)-CH(OH)-CH_3$ 2,3-Butane Diol

$CH_3-C(CH_3)=CH-CH_3 \xrightarrow{HCOOH,\ H_2O}$ $CH_3-C(CH_3)(OH)-C(OH)-CH_3$ 2-methyl-2,3-butane diol

Example No. 12 - Ozonolysis or Ozonization

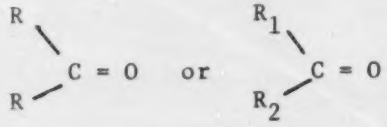


I II III IV

Molozonide (unstable) Ozonide

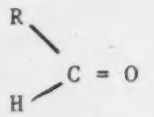
or 1,2,3-Trioxolane

Example No. 12 (continued)



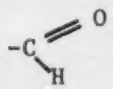
Ketones

(Functional group of the ketones is c = o -carbonyl group)



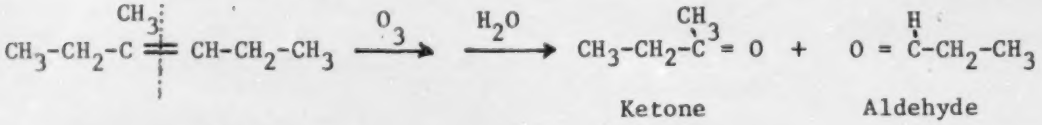
Aldehydes

(Functional group of the aldehydes is

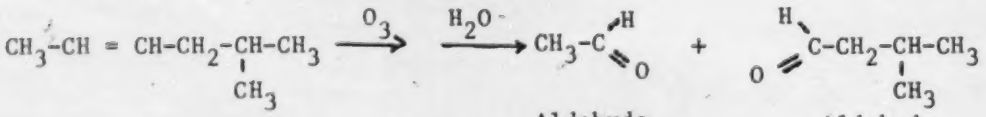


or CHO)

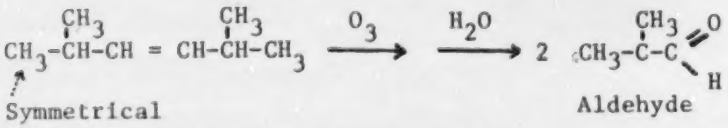
Example No. 13 - Ozonolysis reactions of different alkenes.



Ketone Aldehyde

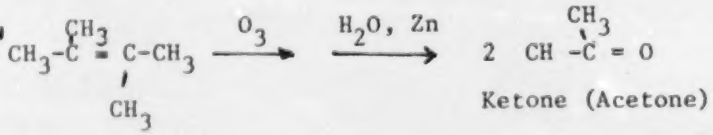


Aldehyde Aldehyde



Symmetrical Alkenes

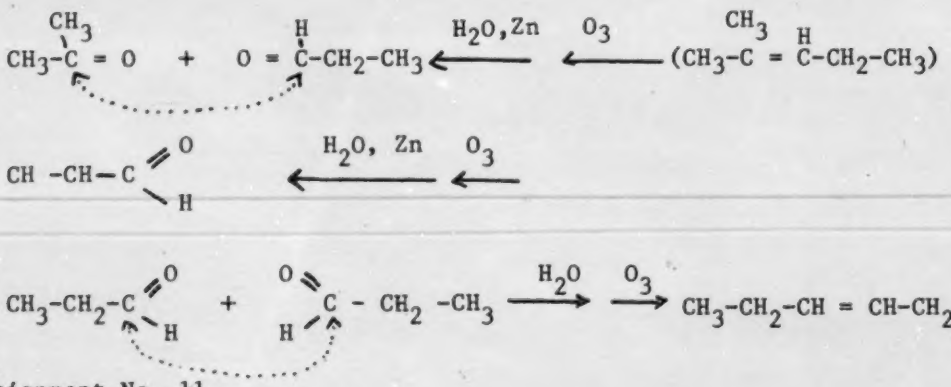
Aldehyde



Ketone (Acetone)

SIP No. 10
Tape 2 - Worksheet

Example No. 14



Assignment No. 11

Complete the following reactions. Draw the structures of the products.

a) 2-methyl-2-butene $\xrightarrow{KMnO_4, aq}$

b) 2-methyl-2-butene $\xrightarrow{O_3}$ $\xrightarrow{H_2O, Zn}$

c) 2-methyl-2-butene $\xrightarrow{HCOOOH,\ H_2O}$

d) 2-pentene $\xrightarrow{O_3}$ $\xrightarrow{H_2O, Zn}$

e) 2,3-dimethyl-2-butene $\xrightarrow{O_3}$ $\xrightarrow{H_2O, Zn}$

f) 2,3-dimethyl-2-butene $\xrightarrow{OsO_4}$ $\xrightarrow{Na_2SO_3}$

g) 4-octene $\xrightarrow{KMnO_4, aq}$

h) 4-octene $\xrightarrow{O_3}$ $\xrightarrow{H_2O, Zn}$

Assignment No. 12

Identify (draw the structure and name) the reactant in the following reactions.

a) $\xrightarrow{KMnO_4, aq}$ 2,3-dimethyl-2,3-pentane diol

SIP No. 10
Tape 2 - Worksheet

Assignment No. 12 (continued)

b) $\xrightarrow{O_3} \xrightarrow{H_2O} CH_3-CH_2-C(H)=O$

c) $\xrightarrow{O_3} \xrightarrow{H_2O} CH(CH_3)-C=O$

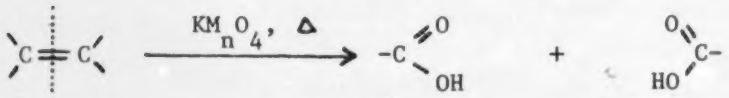
d) $\xrightarrow{\text{Peroxyformic Acid, } H_2O}$ 2,3-butane diol

e) $\xrightarrow{O_3} \xrightarrow{H_2O} CH_3-C(CH_3)-CH=O \quad + \quad CH_3-CH_2-C(CH_3)=O$

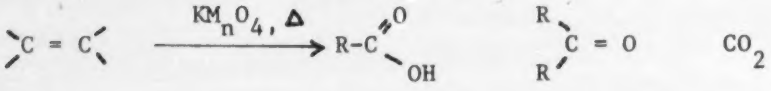
f) $\xrightarrow{O_3} \xrightarrow{H_2O} CH_3-CH_2-C(=O)-H \quad + \quad CH_3-C(CH_3)(CH_3)-C-CH_2-C(=O)-H$

Example No. 15 - Vigorous oxidation with hot KM_nO_4

Carboxylic Acid Functioning Group



$\xrightarrow{KM_nO_4, \Delta}$ $-C(=O)-OH \quad + \quad HO-C(=O)-$



$\xrightarrow{KM_nO_4, \Delta}$ $R-C(=O)-OH$ $\qquad$ $R_2C=O$ $\qquad$ CO_2

Acids $\qquad$ Ketones

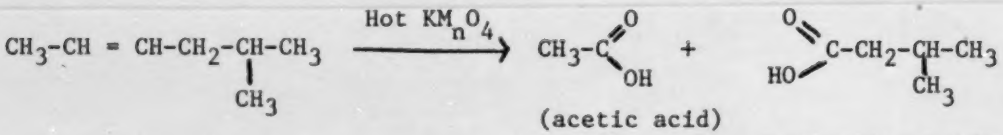
Example No. 16

$CH_3-CH_2-C(CH_3)=CH-CH_2-CH_3 \xrightarrow{\text{Hot } KM_nO_4} CH_3-CH_2-C(CH_3)=O \; + \; HO-C(=O)-CH_2-CH_3$

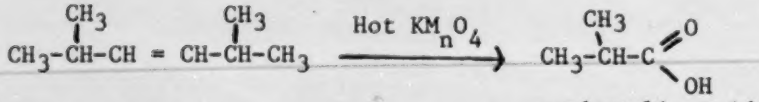
Ketone $\qquad$ Carboxylic Acid (Propanoic Acid)

SIP No. 10
Tape 2 - Work Sheet

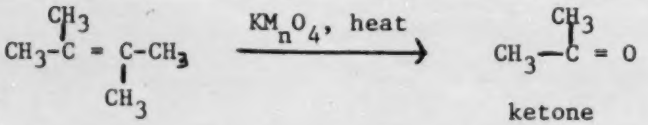
Example No. 16 (continued)



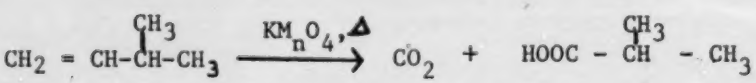
(acetic acid) carboxylic acids



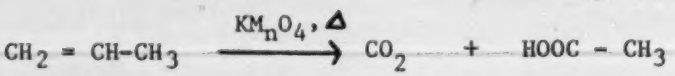
carboxylic acid



ketone



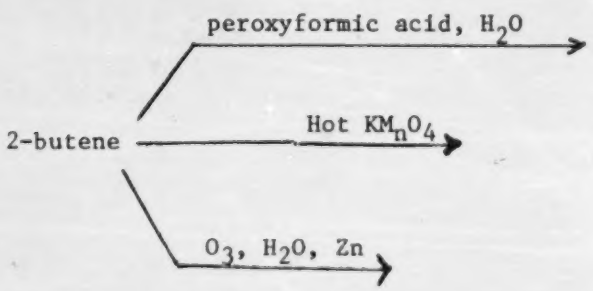
carboxylic acid (2-methyl propanoic acid)



carboxylic acid (acetic acid)

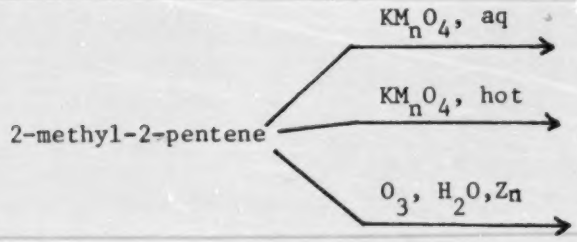
Assignment No. 13

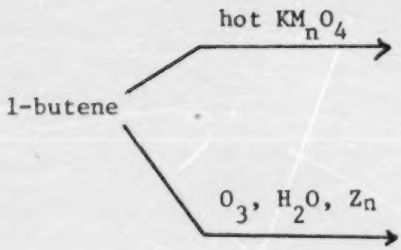
Draw the structure of the products obtained in the following reactions:

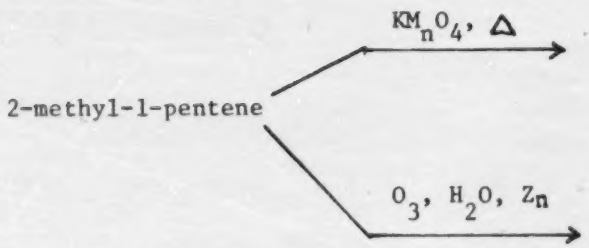


SIP No. 10
Tape 2 - Worksheet

Assignment No. 13 (continued)







Assignment No. 14

Draw the structures and name the reactants and the reagents necessary to produce the following compounds:

a) $\longrightarrow CO_2 + CH_3\,CH_2\,CH_2\,COOH$

butanoic acid

b) $\longrightarrow CH_3-\overset{CH_3}{\overset{|}{C}}=O \quad + \quad CH_3\,CH_2\,C(=O)H$

SIP NO. 10
Tape 2 - Worksheet

c) $\longrightarrow CH_3-CH_2-COOH + CH_3-CH_2-\overset{CH_3}{\underset{|}{C}}=O$

d) $\longrightarrow$ 2-methyl-3,4-hexane diol

e) $\longrightarrow CO_2 + CH_3-\overset{CH_3}{\underset{|}{C}}=O$

Assignment No. 15

Outline all steps in a possible laboratory synthesis of 2,3-dimethyl-2,3-butane diol from propane.

Self Instructional Package No. 10
Tape 2 - Answer Sheet

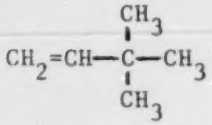
ALKENES - REACTIONS II

HYDROGENATION, POLYMERIZATION, OXIDATION

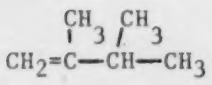
Assignment No. 1

2-Pentene has lower heat of hydrogenation. It possesses less energy and is therefore MORE stable.

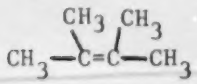
Assignment No. 2



$(CH_2=CHR)$ 30.3 kcal/mole min. stability

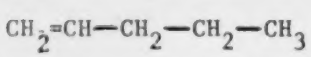


$(CH_2=CR_2)$ 28 kcal/mole

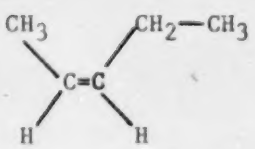


$(R_2C=CR_2)$ 26.6 kcal/mole max. stability

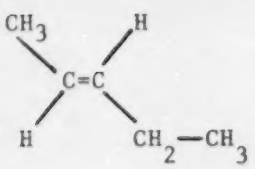
Assignment No. 3



806.9 kcal/mole



805.3 kcal/mole

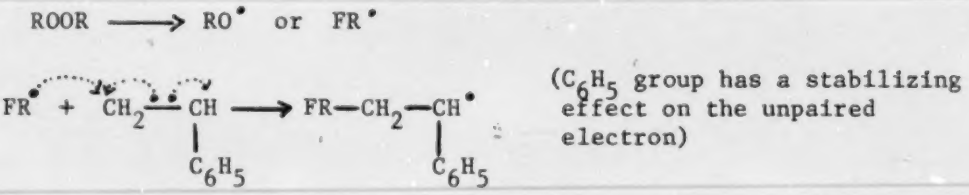


804.3 kcal/mole

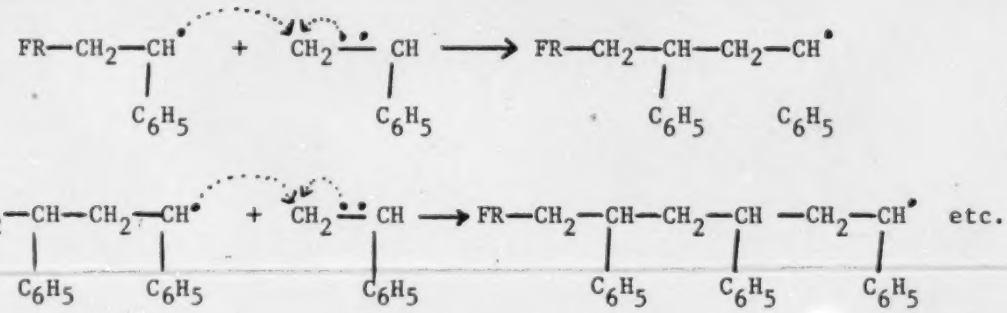
SIP #10
Tape 2 - Answer Sheet

Assignment No. 4 - Free Radical Polymerization of styrene.

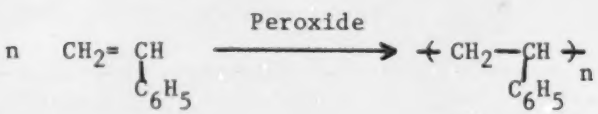
Chain initiation



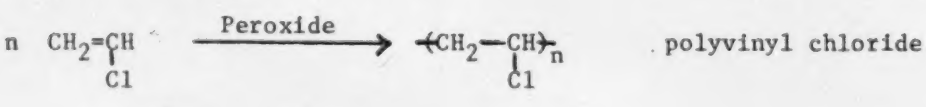
Chain propagation

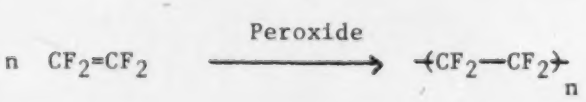


Overall reaction



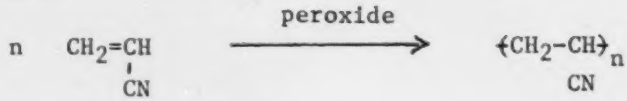
Assignment No. 5



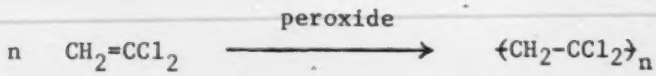


SIP No. 10
Tape 2 - Answer Sheet

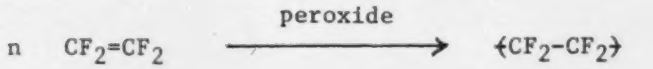
Assignment No. 6



orlon

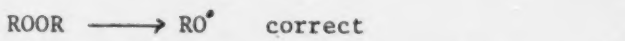


saran

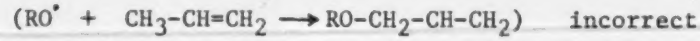


teflon

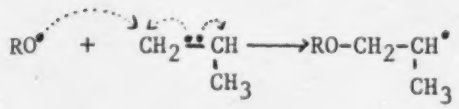
Assignment No. 7



correct

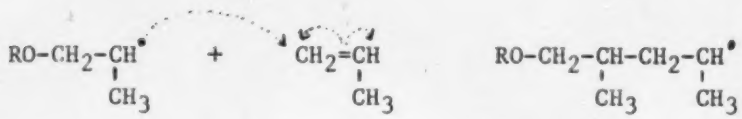


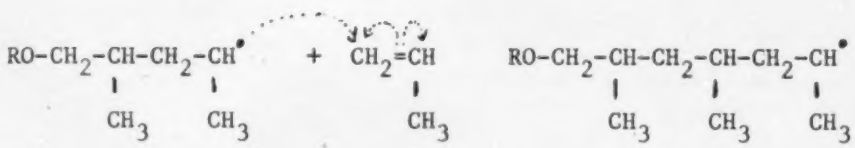
incorrect



correct

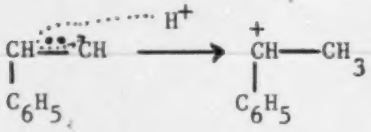
(only doubly bonded carbon are involved in the reaction. All alkyl groups become branches)





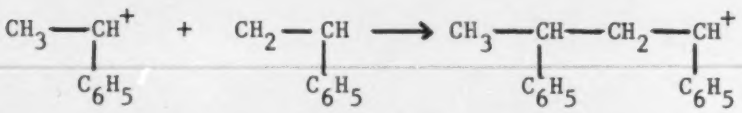
SIP #10
Tape 2 - Answer Sheet

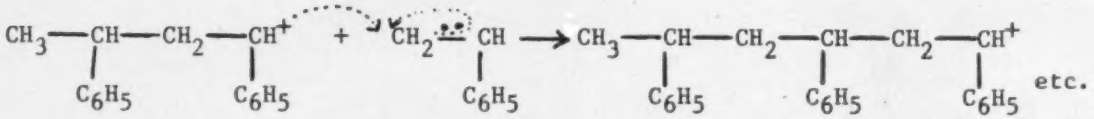
Assignment No. 8 (continued)



correct

(C_6H_5 has a stabilizing effect on the carbonium ion. The positive charge is delocalized over C_6H_5 group.)





etc.

Assignment No. 9

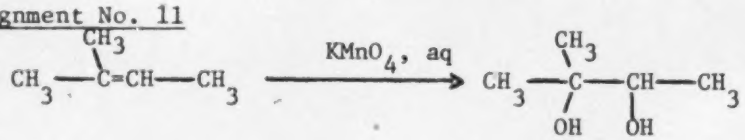
Alkyl groups have a stabilizing effect on the intermediate carbonium ion or the retermediate free radical. More stable intermediate is formed faster, therefore, the orientation will always be the same.

Assignment No. 10

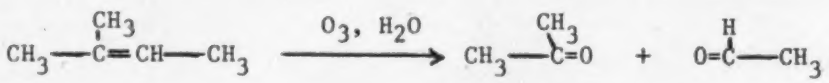
Cl is an electron withdrawing group. It has considerably higher electronegativity than the carbon atom it is attached to. Consequently, chlorine bonded to the carbon atom bearing a positive charge destabilizes the carbonium ion. The correct mechanism therefore is II.

Assignment No. 11

a.)

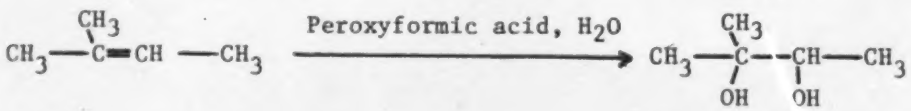


b.)



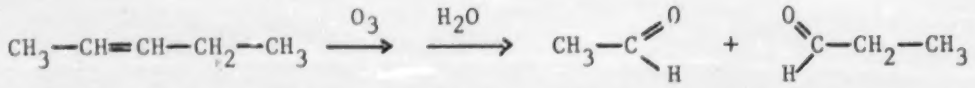
ketone aldehyde

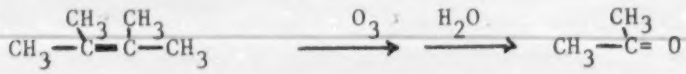
c.)

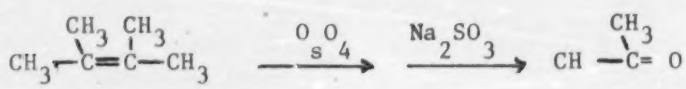


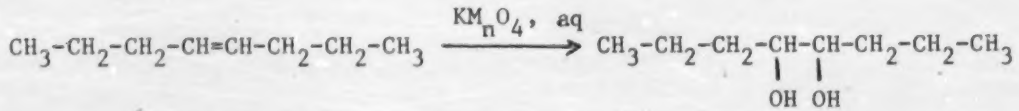
SIP #10
Tape 2 - Answer Sheet

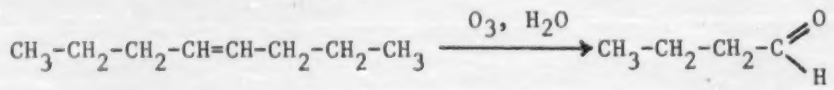
Assignment No. 11 (continued)

d.) 

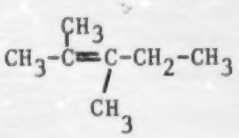
e.) 

f.) 

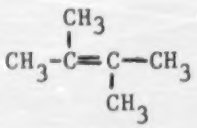
g.) 

h.) 

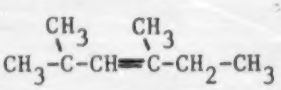
Assignment No. 12

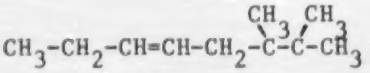
a.) 2,3-dimethyl-2-pentene 

b.) 3-hexene $CH_3-CH_2-CH=CH-CH_2-CH_3$

c.) 2,3-dimethyl-2-butene 

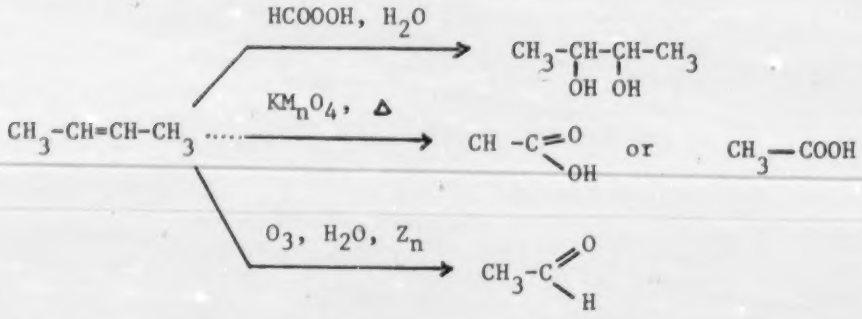
d.) 2-butene $CH_3-CH=CH-CH_3$

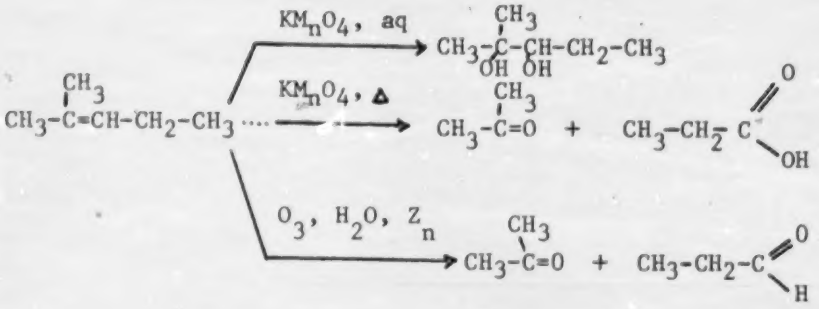
e.) 2,4-dimethyl-3-hexene 

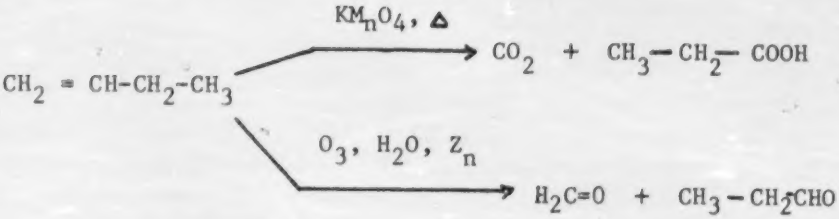
f.) 6,7-dimethyl-3-octene 

SIP #10
Tape 2 - Answer Sheet

Assignment No. 13







Assignment No. 14

a.) $CH_2=CH-CH_2-CH_2-CH_3$ $\xrightarrow{KMnO_4, \Delta}$ CO_2 + $HOOC-CH_2-CH_2-CH_3$

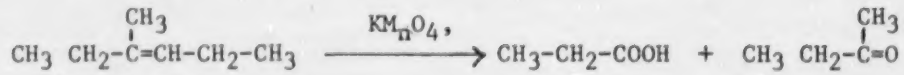
2-pentene

b.) $CH_3-C(CH_3)=CH-CH_2-CH_3$ $\xrightarrow{O_3, H_2O, Zn}$ $CH_3-C(CH_3)=O$ + $CH_3CH_2C(=O)H$

2-methyl-2-pentene

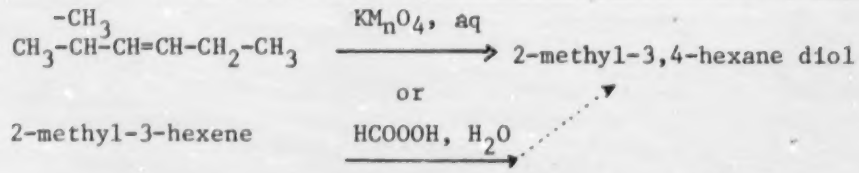
Assignment No. 14 (continued)

c.)



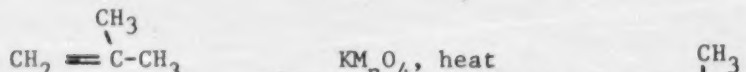
3-methyl-3-hexene

d.)



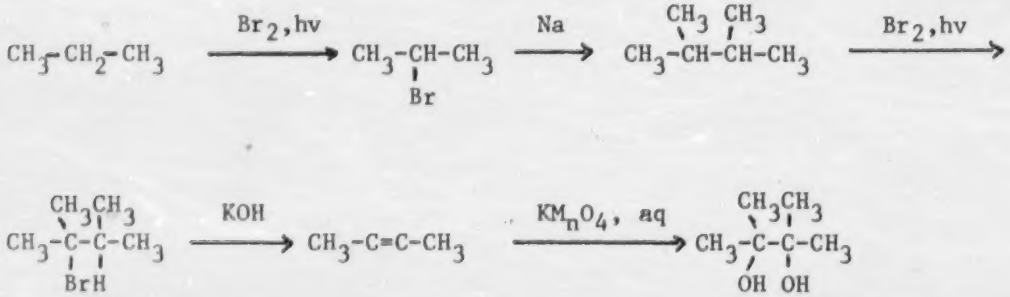
2-methyl-3-hexene

e.)



2-methyl-1-propene

Assignment No. 15



Self Instructional Package No. 10
Form D - Progress Check Evaluation

ALKENES - REACTIONS II

Identify the statements below as true or false by placing a capital T or F in the space provided.

1. _____ Resonance effect is the reason for the great stability of the allylic free radical.

2. _____ High heat of hydrogenation means low stability of the alkene.

3. _____ Platinum decreases the energy of activation in the hydrogenation reaction.

4. _____ Surface catalysis takes place in a liquid phase.

5. _____ Hyperconjugation is the delocalization of electrons involving the π orbitals.

6. _____ 2-methyl-2-butene is more stable than the 2-methyl-1-butene.

7. _____ 3-methyl-1-pentene has lower heat of hydrogenation than 2-methyl-1-pentene.

8. _____ Peroxide can be used to initiate a polymerization reaction.

9. _____ NBS is used to catalyze the addition of halogens to alkenes.

10. _____ Bayer test is the reaction of alkenes with aqueous KM_nO_4.

Blacken out the correct answer or answers in each question.

11. The initiators usually used in the cationic polymerization reaction are:

    a) sulfuric acid H_2SO_4

    b) buron trifluoride BF_3

    c) hydrogen fluoride HF

    d) peroxide, light

12. The correct statements about the allylic free radical are:

    a) it is more stable than the vinyl free radical

    b) it has lower energy than the vinyl free radical

    c) it is stabilized by the delocalization of electrons involving the bond

    d) it is stabilized by the hyperconjugation effect

13. The product of the peroxide catalyzed reaction of chloroform with 3-methyl-2-pentene is:

    a) 1,1,1-trichloro-3-methyl-hexane

    b) 1,1,1-trichloro-2-methyl-2-ethyl butane

    c) 1,1,1-trichloro-3-methyl pentane

    d) 1,1,1-trichloro-2,3-dimethyl pentane

14. The product of the peroxide catalyzed reaction of 2-methyl-2-butene with carbontetrabromide is:

    a) 1,1,1,3-tetrachloro-2,3-dimethyl butane

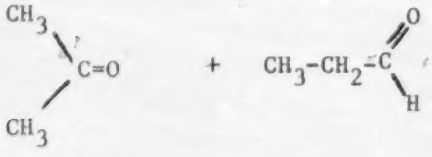
    b) 1,1,1,2-tetrachloro-2-methyl pentane

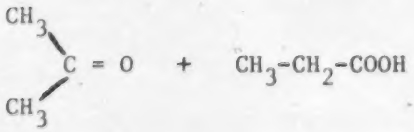
    c) 1,1,1,3-tetrachloro-2,2-dimethyl butane

    d) 1,1,1,4-tetrachloro-4-methyl pentane

15. The reaction of 2-methyl-2-pentene with peroxyformic acid, followed by hydrolysis will yield:

    a) 2-methyl-2,3-pentane diol

    b) 

    c) 

    d) $CH_3COOH + CH_3-CH_2-COOH$

16. Identify the reagents that will convert propene into 1,2-propane diol.

a) $KMnO_4$, H_2O

b) O_3, H_2O

c) peroxyformic acid, H_2O

d) OsO_4, Na_2SO_3

17. Identify the alkene which will yield compounds I and II when treated with hot $KMnO_4$.

I

II

a) 3-methyl-4-heptene

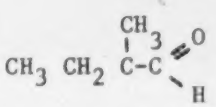
b) 2,4-dimethyl-2-hexene

c) 2,5-dimethyl-2-hexene

d) 2,3-dimethyl-2-pentene

18. The alkene that will yield compounds I and II upon ozonolysis followed by hydrolysis is:

I



II

a) 4-methyl-1-pentene

b) 3-methyl-1-pentene

c) 3-methyl-3-pentene

d) 2-methyl-1-pentene

SIP #10
Form D - Progress Check Evaluation

19. Identify the reagents that can be used in a multi-step laboratory synthesis to convert butane to 3-methyl-2,3-pentane diol.

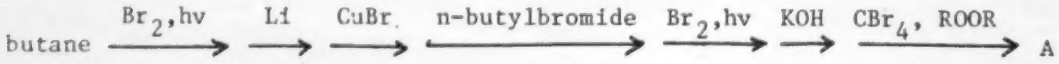
a) Br_2,hv; Na; Br_2,hv; KOH; KM_nO_4, H_2O

b) Br_2,hv; Li; CuBr; ethylbromide; Br_2,hv; KOH; peroxyformic acid, H_2O

c) Br_2,hv; Na; KOH; peroxyformic acid, H_2O

d) Br_2,hv; Li; CuBr; propylbromide; Br_2,hv; KOH; KM_nO_4, H_2O

20. Identify product A obtained in a multi-step synthetic sequence below.



a) 1,1,1,3-tetrabromo-3-methyl-2-propyl pentane

b) 1,1,1,3-tetrabromo-2,3-dimethyl-heptane

c) 1,1,1,4-tetrabromo-4-methyl-octane

d) 1,1,1,3-tetrabromo-2-methyl-2-ethyl hexane

Self Instructional Package No. 10
Form B[1] - Answer Sheet

ALKENES - REACTIONS II

1. T
2. F
3. T
4. T
5. T
6. F
7. F
8. F
9. T
10. T
11. a, d
12. d
13. a,b,c
14. b
15. a
16. c
17. b
18. d
19. b
20. b
21. d
22. b, c
23. c

Self Instructional Package No. 10
Form D1 - Answer Sheet

ALKENES - REACTIONS II

1.	T	11.	a, b, c
2.	T	12.	a, b, c
3.	T	13.	d
4.	F	14.	a
5.	F	15.	a
6.	T	16.	a, c, d
7.	F	17.	b
8.	T	18.	b
9.	F	19.	b
10.	T	20.	a, b